Technical Report EL-98-8
August 1998

US Army Corps of Engineers
Waterways Experiment Station

Feasibility of Using Natural Attenuation as a Remedial Alternative for Explosives-Contaminated Groundwater at Site L1, Joliet Army Ammunition Plant, Joliet, Illinois

by Judith C. Pennington, Danny W. Harrelson, Mansour Zakikhani, Douglas Gunnison, Joan U. Clarke, Christian J. McGrath, Herbert Fredrickson, James H. May, WES

Ed Perkins, Charolett A. Hayes, AScI

David Ringelberg, DynTel

Prepared for U.S. Army Industrial Operations Command

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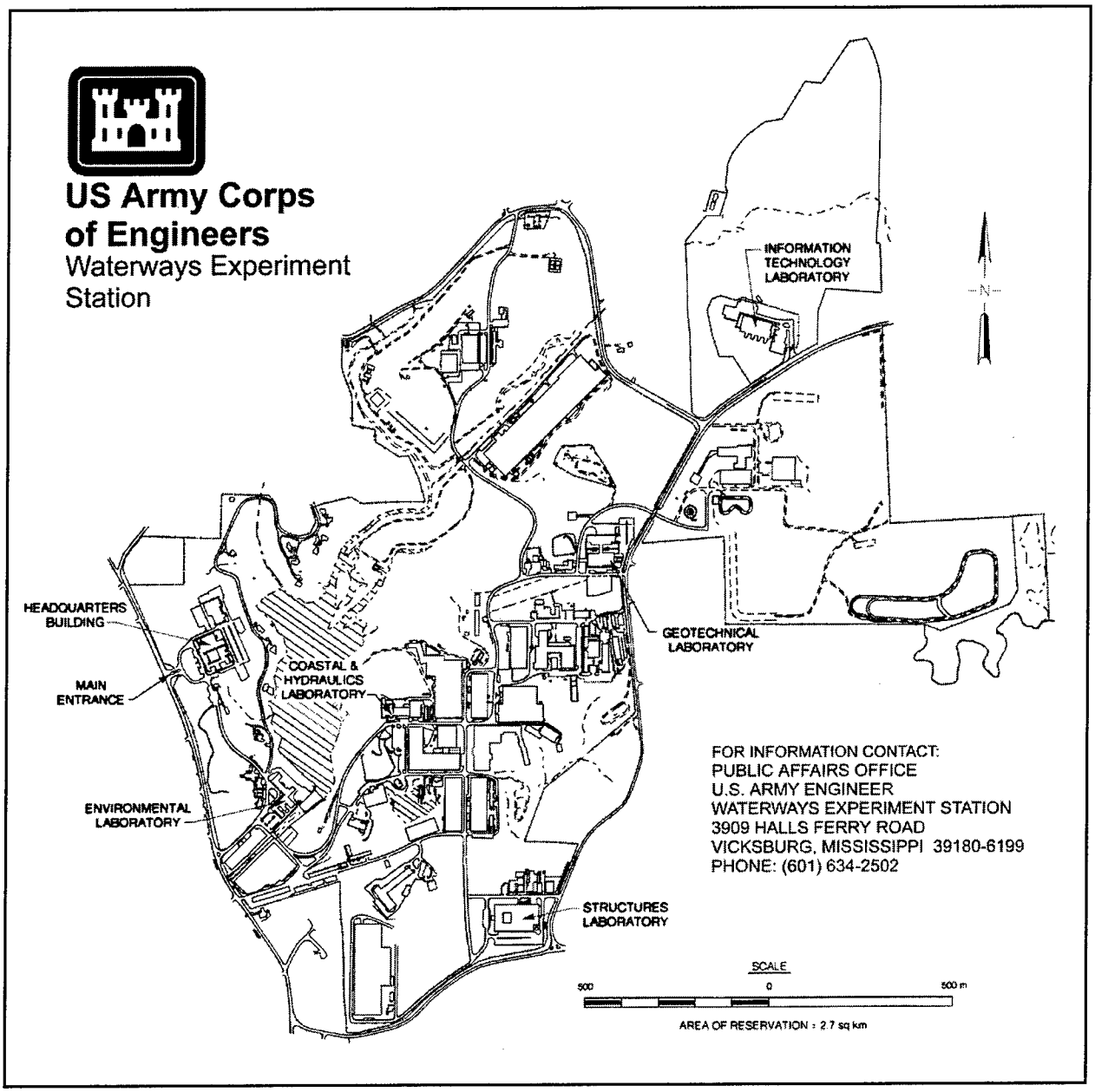

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Preface

The report herein was prepared for the U.S. Army Industrial Operations Command (IOC), Rock Island, IL, by the Environmental Laboratory (EL) and the Geotechnical Laboratory (GL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS, in association with AScI Corporation, McLean, VA, and DynTel, Vicksburg, MS. The research was conducted in support of the Joliet Army Ammunition Plant, Site L1. The Principal Investigators and authors of this report were Drs. Judith C. Pennington, Douglas Gunnison, and Herbert Fredrickson, Ecosystem Processes and Effects Branch, Environmental Processes and Effects Division (EPED), EL; Dr. Mansour Zakikhani and Mr. Christian J. McGrath, Water Quality and Contaminant Modeling Branch (WQCMB), EPED; Ms. Joan U. Clarke, Fate and Effects Branch (FEB), EPED; and Mr. Danny W. Harrelson and Dr. James H. May, Engineering Geology Branch (EGB), Earthquake Engineering and Geosciences Division (EEGD), GL. Also serving as authors and providing support for biomarker research were Dr. Ed Perkins and Mrs. Charolett A. Hayes, AScI, and Mr. David Ringelberg, DynTel. Explosives analyses were performed by Mrs. Lynn Escalon, AScI, in the Environmental Chemistry Branch, Environmental Engineering Division, EL. Project monitors were Messrs. Andrew Poppen and Cyril Onewokae, IOC. The cone penetrometry sampling event and the subsequent biomarker and stable isotope research were sponsored by the Strategic Environmental Research and Development Program, Washington, DC, under Project 1043.

The report was reviewed by Drs. James M. Brannon and William Davis, EL. The study was conducted under the direct supervision of Dr. Mark S. Dortch, Chief, WQCMB; Dr. Bobby L. Folsom, Jr., Chief, FEB; and Mr. William L. Murphy, Chief, EGB; and under the general supervision of Dr. Richard E. Price, Chief, EPED; Dr. Lillian D. Wakely, Chief, EEGD; Dr. John Harrison, Director, EL; and Dr. William F. Marcuson III, Director, GL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Robin R. Cababa, EN.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic yards	0.7645549	cubic meters
feet	0.3048	meters
gallons (U.S. liquid)	3.785412	liters
inches	2.54	centimeters
miles (U.S. statute)	1.609347	kilometers

1 Introduction

Background

Natural attenuation may be an attractive alternative to more expensive remediation technologies at sites that meet well-defined selection criteria, acceptable risk levels, and that satisfy specific regulatory concerns. Environmental remediation technology is necessarily evolving toward less expensive, less intrusive, long-term solutions. Natural attenuation may be a legitimate and sensible alternative to other remediation methods if appropriate evidence of protection for potential contaminant receptors is documented. A recent study by the U.S. Army Engineer Waterways Experiment Station (WES) verified a regulatory attitude of potential acceptance of natural attenuation for explosives-contaminated sites (Balasco et al. 1996). This study confirmed that most regulatory agencies would accept natural attenuation given appropriate scientific, engineering, and risk assessment data.

A significant precedent for natural attenuation of environmental contaminants has been set by the widely implemented protocol for natural attenuation of fuels that was developed by the Air Force Center for Environmental Excellence (AFCEE) (Weidemeir et al. 1995a,b). The protocol has been implemented at more than 60 sites nationwide. The protocol espouses development of three lines of evidence for natural attenuation: (a) documented loss of contaminants at the field scale, (b) the use of chemical analytical data in mass balance calculations, and (c) laboratory microcosm studies using aquifer samples collected from the site.

In December 1997, the U.S. Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response released a policy statement titled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (EPA 1997). The directive emphasizes source control, monitoring, and use of the following "three lines of evidence," which are similar to those developed in the AFCEE protocol for fuels:

a. Historical groundwater and/or soil chemistry data that demonstrate a clear meaningful trend of declining contaminant mass and/or concentrations at appropriate monitoring or sampling points.

b. Hydrogeologic or geochemical data that can be used to indirectly demonstrate the type(s) of natural attenuation processes active at the site and the rate at which such processes will reduce contaminant concentrations to required levels.

c. Data from field or microcosm studies (conducted in or with actual contaminated site media) that directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

The directive includes various "physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water." The directive is risk-based and requires planning of "contingency remedies" should natural attenuation prove less effective than anticipated.

The Army has also circulated an interim policy statement on natural attenuation (*Federal Register* 1990). This statement mandates that natural attenuation be at least considered for remediation of all contaminated Army sites.

Rationale

Natural attenuation of explosives occurs through one or more of the following mechanisms: (a) microbial mineralization to very simple, nonhazardous inorganic compounds, (b) microbial transformation to similar or more complex, but innocuous, compounds, (c) immobilization due to interactions with the soil or aquifer, and (d) immobilization due to restrictive site geology and/or hydrology. Under the special condition of extreme site isolation, natural attenuation may also be acceptable if receptor risk is sufficiently low. Mineralization of 2,4,6-trinitrotoluene (TNT) to simple inorganic compounds, such as carbon dioxide and nitrogen, occurs at a slow rate and to a limited extent in natural soils and aquifers (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"). However, immobilization of reduction products of TNT in soils is often rapid and extensive (Brannon, Price, and Hayes 1998; Price, Brannon, and Yost, in preparation). For this reason, the attenuation of TNT may best be demonstrated through geochemical immobilization processes rather than microbial degradation processes alone. For 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX), immobilization is less significant, but microbial degradation is promising. The microbial degradation pathway for RDX is less well defined than the pathway for TNT reduction, but degradation of RDX under reduced conditions has been confirmed in soils (McCormick, Cornell, and Kaplan 1981; Price, Brannon, and Yost, in preparation).

Objectives

Specific objectives of the study included the following:

a. Demonstrate that natural attenuation of explosives is occurring at Site L1.

b. Estimate the attenuation rate and correlate it with the site hydrogeologic regime.

c. Define reaction pathways and determine product balances with selected soils and aquifer materials.

d. Represent graphically the monitoring data generated for Site L1.

e. Generate a three-dimensional model conceptualization and numerically simulate long-term attenuation of explosives at Site L1.

2 Site Description and Historical Perspective

Site Function and Evolution

The Joliet Army Ammunition Plant (JAAP) was constructed in the early 1940s in Will County, Illinois, about 17 miles[1] south of Joliet (Figure 1). The plant functioned in production and load-assemble-package (LAP) of explosives. The JAAP is a government-owned, contractor-operated installation currently maintained in nonproducing status. The JAAP was used extensively during World War II. In August of 1945, production of explosives halted; the sulfuric acid and ammonium nitrate plants were leased; and remaining production facilities were placed in layaway status. The explosives manufacturing area was reactivated during the Korean Conflict (1953 to 1957) and again for Vietnam (1965 to 1969). Production gradually decreased until it was stopped in 1977. Currently, various tracts of land in the 30,000-acre site are transitioned to the Department of Interior as part of the National Tall Grasslands program. Additional tracts are being farmed. During the Installation Assessment and Installation Restoration Surveys, site conditions suggested the potential for contamination from past operations (Donohue and Associates 1982a,b). Subsequent studies identified contamination in the groundwater, surface water, soil, and sediment at the LAP areas (Dames and Moore, Inc. 1986). The LAP area was placed on the National Priority List in April 1989, and the site was designated a Superfund site. A Remedial Investigation (RI) identified 35 specific study sites in the LAP area as potentially contaminated (Dames and Moore, Inc. 1993).

Site L1 functioned from 1941 to 1945 in defusing of munitions, removal of explosives from shells and recycling of casings, crystallization of ammonium nitrate, and TNT recovery (Figure 2). From 1946 through 1952, the site functioned in reclamation of TNT from shells (Dames and Moore, Inc. 1996). The principal source of explosives contamination at Site L1 is a ridge and furrow system (10 acres) that received process wastewater from washout operations

[1] A table of factors for converting non-SI units of measurement to SI units is presented on page ix.

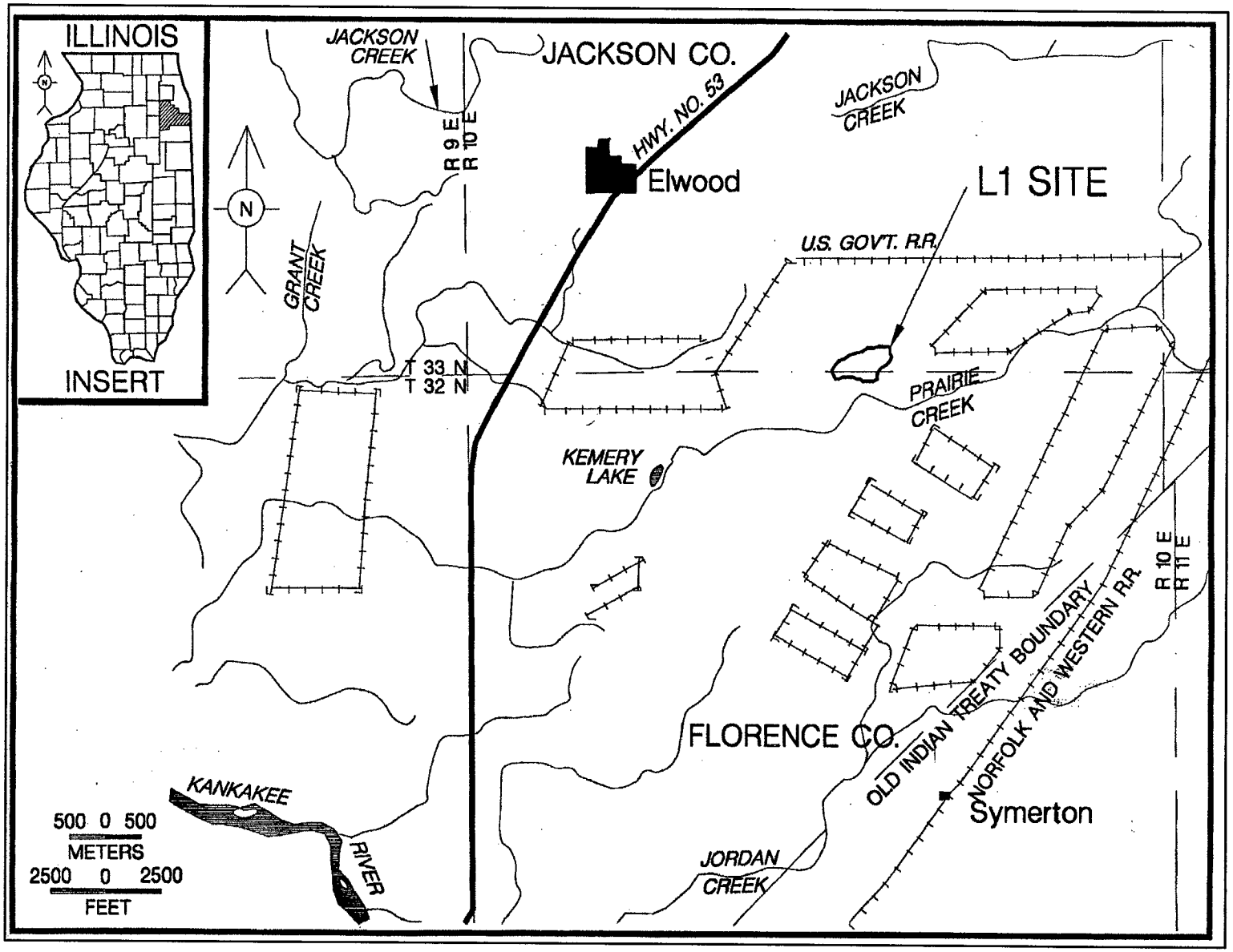

Figure 1. Location of Site L1, Joliet Army Ammunition Plant, Joliet, IL

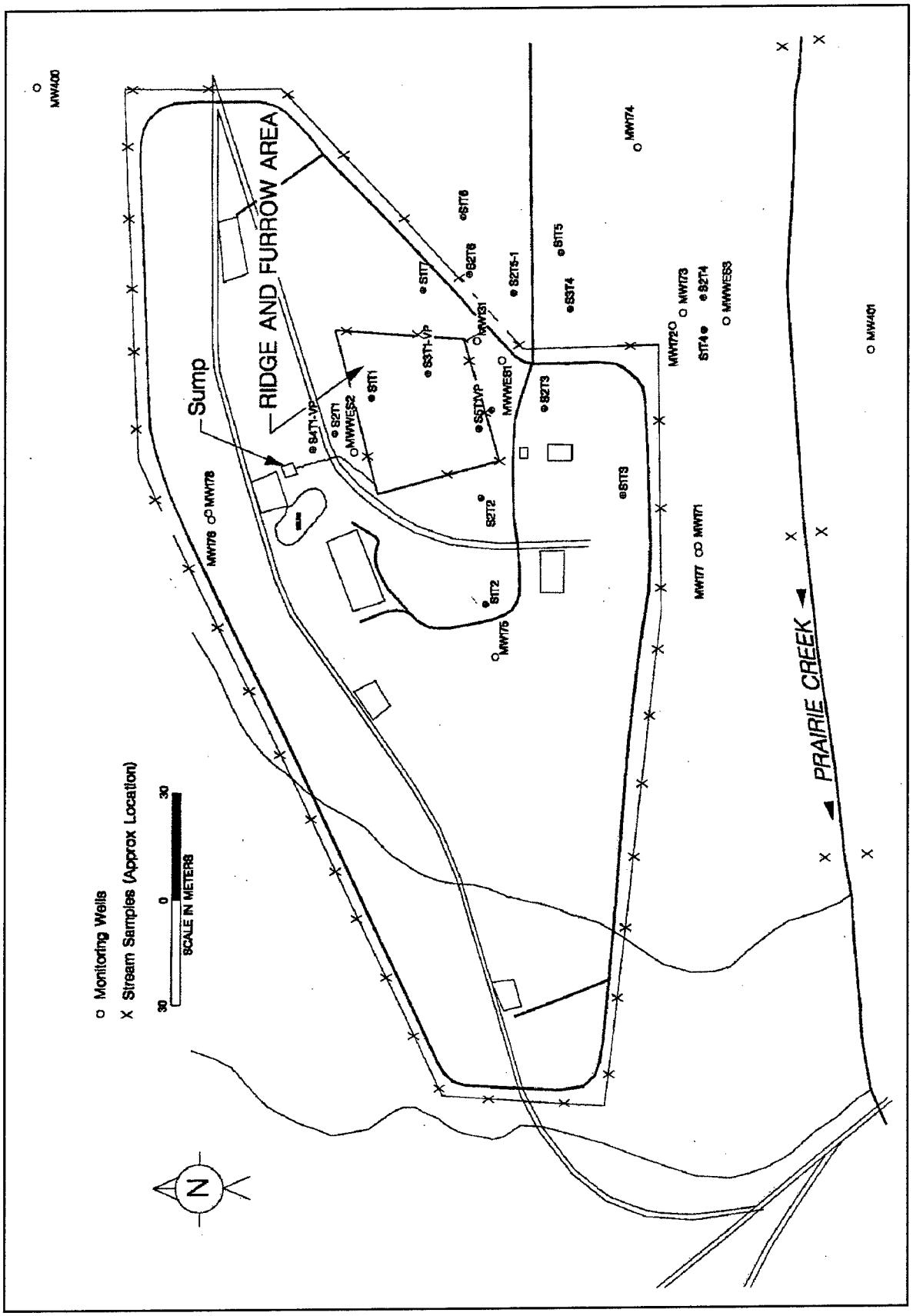

Figure 2. Site L1, Joliet Army Ammunition Plant

(Dames and Moore, Inc. 1993). Extensive additional site history is given in the Feasibility Study, Ground Water Operable Unit (Dames and Moore, Inc. 1996), and in the Phase 1 Remedial Investigation Results Report, Load-Assemble-Package (LAP) Area (Dames and Moore, Inc. 1993).

Physiography and Geology

Joliet Army Ammunition Plant is located within the northern portion of the Central Lowlands physiographic province. This province is characterized by relatively flat topography and low relief. The most prominent topographic feature of JAAP is a 50-ft-high glacial escarpment that trends north-south across the installation. The installation is drained by four streams: Grant Creek, Prairie Creek, Jordan Creek, and Spoil Bank Creek.

Regionally, JAAP is located on a large structural high called the Kankakee Arch. This feature is located between the Michigan Basin to the northeast and the Illinois Basin to the south. Faulting in the area includes the Sandwich Fault Zone, which trends northwest-southeast through the eastern portion of JAAP. Structural contour maps indicate that vertical displacement of the fault increases with depth and that the fault may affect groundwater flow locally (Kolata, Bushbash, and Treworgy 1978; U.S. Army Environmental Hygiene Agency 1977). However, no regional effects have been observed (Viscocky 1985; Suter et al. 1959).

Site L1, Group 61 covers approximately 80 acres in the north-central portion of the LAP area (Figures 1 and 2). The site has been contaminated by the use of a 10-acre ridge and furrow system, i.e., an evaporating bed, that received process wastewater from washout operations. Ground surface elevations at Site L1 vary from 650 ft above MSL (mean sea level) along the northern border to approximately 610 ft above MSL along Prairie Creek to the south. Surface runoff flows into three drainage ditches that ultimately flow into Prairie Creek. Prairie Creek in the vicinity of Site L1 is 10 to 15 ft wide and flows from east to west.

The soils at Site L1 are glacial materials composed of very fine-grained silts and clays with various amounts of erratically occurring materials such as cobbles and boulders. These materials were deposited as outwash during the waning stages of continental glaciation. The glacial materials lie unconformably on bedrock, which consists of tan to greenish gray thinly bedded Silurian age dolomitic sandstone. The sandstone is highly fractured and weathered near its contact with the overlying glacial deposits and has solution features in the upper portion of the section. In general, the fractures and degree of weathering in the sandstone decrease with depth.

Hydraulic conductivities are generally very low. A hydraulic conductivity of 9.2×10^{-6} cm sec^{-1} was reported for MW131 (Donohue and Associates 1982), which is completed in the glacial till (described as overburden in Dames and Moore, Inc. 1994). Hydraulic conductivities for these materials are typically

low, while conductivities in the bedrock are much higher. The high bedrock conductivities are attributed to solution features in the upper portions of the bedrock. Using slug test data, a hydraulic conductivity of 4.9×10^{-4} cm sec^{-1} was calculated for the bedrock (Dames and Moore, Inc. 1994). Based on these conductivity values, groundwater flow velocities were estimated at 35 and 16 ft $year^{-1}$ for the bedrock and glacial till, respectively. The approximate direction of groundwater movement is to the southwest in the deep wells and southeast in the shallow wells (Dames and Moore, Inc. 1994).

Historical Contaminant Data

Soils

Results of soil sampling in 1981 revealed TNT (up to 14,500 $\mu g\ g^{-1}$) and 1,3,5-trinitrobenzene (TNB) in the southern portion of the ridge and furrow system (Dames and Moore, Inc. 1993). Samples taken in 1991 from the northern and central portions were lower, 0.54 - 110 μg TNT g^{-1} and 0.71 - 12.0 μg TNB g^{-1}. Erosion and transport, biodegradation, and sample variability were suggested to account for the difference over the 10-year time period. Estimates of the volume of contaminated soil requiring remediation were 5,925 cu yd (to a depth of 1 ft). Exceedance of the preliminary remedial goal (PRG) for TNT of 290 $\mu g\ g^{-1}$ occurred throughout the ridge and furrow system, but occurred below 1 ft in depth in only one sample, which was located in the southeastern corner (Dames and Moore, Inc. 1993).

High levels of explosives were also observed in soils near the washout building and sump in 1991. The total volume of soil recommended for remediation in this area was 6,010 cu yd. Prairie Creek was also checked for explosives, but none were detected (Dames and Moore, Inc. 1993).

Groundwater

Between 1986 and 1991, groundwater data were collected five times in Site L1 (Dames and Moore, Inc. 1993). The following six explosives were detected in exceedance of the PRGs: TNT, TNB, RDX, 2,4-dinitrotoluene (2,4DNT), 2,6-dinitrotoluene (2,6DNT), and 1,3-dinitrobenzene (DNB) (Table 1). All of the PRG exceedances were in Wells MW131, MW172, and MW173 (Dames and Moore, Inc. 1993). Detections of 2,4DNT and 2,6DNT were low, 2.01 and 8.54 $\mu g\ L^{-1}$, respectively.

Past Remedial Actions

Between 1994 and 1995, Argonne National Laboratory conducted a field demonstration of slurry reactor biotreatment of explosives-contaminated soils at

Table 1
Historical Groundwater Concentrations ($\mu g\ L^{-1}$) of Explosives and Degradation Products for Site L1, Joliet Army Ammunition Plant[1]

Well No.	Date	TNB	DNB	TNT	2,4DNT	2,6DNT	HMX	RDX	Tetryl
MW131	06/10/81	1,291.00[2]	NT[3]	2,250.000	1.29[2]	3.75[2]	NT	NT	NT
	1983	NT	NT	NT	NT	NT	NT	NT	NT
	11/15/85	1,610.000	5.000	2,150.000	2.010	4.140	NT	7.00 DL[4]	58.600
	04/22/86	755.000	2.300 DL	576.000	0.560 DL	8.540	NT	7.00 DL	21.700
	08/21/91	1,300.000	0.611 DL	1,900.000	0.064 DL	0.074 DL	1.210 DL	38.600	2.490 DL
MW172	3/9/83	9.200	NT	40.800	0.280 DL	3.00 DL	NT	NT	NT
	9/28/83	2.800 DL	NT	10.600	0.280 DL	3.000 DL	NT	NT	NT
	10/30/85	3.080	2.300 DL	16.200	0.560 DL	1.200 DL	NT	14.200	5.600 DL
	0/14/86	3.840	2.300 DL	12.900	0.560 DL	1.200 DL	NT	7.220	5.600 DL
	08/23/91	0.449 DL	0.611 DL	2.340	0.064 DL	0.074 DL	1.210 DL	8.790	2.490 DL
MW173	03/09/83	6.870	NT	50.300	0.280 DL	3.000 DL	NT	NT	NT
	09/28/83	2.800 DL	NT	68.400	0.280 DL	3.000 DL	NT	NT	NT
	10/31/85	14.00	2.30 DL	105.00	0.560 DL	1.200 DL	NT	56.500	5.600 DL
	04/14/86	2.090	2.300 DL	11.00	0.560 DL	1.200 DL	NT	8.000	5.600 DL
	08/23/91	5.308	0.611 DL	55.000	0.064 DL	0.074 DL	43.800	42.100	2.490 DL
MW174	03/09/83	2.800DL	NT	0.310 DL	0.280DL	3.000DL	NT	NT	NT
	09/28/83	2.800DL	NT	0.610	0.280DL	3.000DL	NT	NT	NT
	10/31/85	1.400DL	2.300DL	1.900DL	0.560DL	1.200DL	NT	7.000DL	5.600DL
	04/14/86	1.400DL	2.300DL	1.900DL	0.560DL	1.200DL	NT	7.000DL	5.600DL
MW174	08/23/91	0.449 DL	0.611 DL	0.635 DL	0.064 DL	0.074 DL	1.210 DL	1.170 DL	2.490 DL
MW175	03/10/83	2.800 DL	NT	0.310 DL	0.280 DL	3.000 DL	NT	NT	NT
	04/14/86	1.400 DL	2.300 DL	1.900 DL	0.560 DL	1.200 DL	NT	7.000 DL	5.600 DL
	11/13/91	0.449 DL	0.611 DL	0.635 DL	0.064 DL	0.074 DL	1.210 DL	1.170 DL	2.490 DL
MW177	03/09/83	2.800 DL	NT	0.310	0.280 DL	3.000 DL	NT	NT	NT
	09/28/83	2.800 DL	NT	0.310	0.280 DL	3.000 DL	NT	NT	NT
	10/30/85	1.400 DL	2.300 DL	1.900 DL	0.560 DL	1.200 DL	NT	7.000 DL	5.600 DL
	04/14/86	1.400 DL	2.300 DL	1.900 DL	0.560 DL	1.200 DL	NT	7.000 DL	5.600 DL

(Continued)

[1] Dames and Moore, Inc. (1993).
[2] Mean of two samples collected in duplicate.
[3] Not tested.
[4] Detection limit.

Table 1 (Concluded)									
Well No.	Date	TNB	DNB	TNT	2,4DNT	2,6DNT	HMX	RDX	Tetryl
	08/23/91	0.449 DL	0.611 DL	0.635 DL	0.064 DL	0.074 DL	1.210 DL	1.170 DL	2.490 DL
MW178	03/09/83	2.800 DL	NT	0.380	0.280 DL	3.000 DL	NT	NT	NT
	11/06/85	1.400 DL	2.300 DL	1.900 DL	0.560 DL	1.200 DL	NT	7.000 DL	5.600 DL
	04/14/86	1.400 DL	2.300 DL	1.900 DL	0.560 DL	1.200 DL	NT	7.000 DL	5.600 DL
	08/21/91	0.449 DL	0.611 DL	0.635 DL	0.064 DL	0.074 DL	1.210 DL	1.170 DL	2.490 DL

Site L1 (Manning, Boopathy, and Breyfogle 1996). Soils for the demonstration were removed from the ridge and furrow system. After the demonstration, treated soils were left on the site.

Between 1993 and 1995, a plant uptake study was conducted at Site L1 (Zellmer et al. 1995). The study consisted of a plant and soil survey for explosives and a cropping experiment using two plant species grown in soils amended with three levels of chopped grass hay. The cropping experiment was established on a 16- by 24-m plot in the ridge and furrow system (high-TNT area) and a plot of the same size west of the ridge and furrow system (intermediate-TNT area). Results indicated no TNT nor transformation products in aboveground plant tissues of existing or cropped vegetation, but low concentrations associated with the roots. Crop health was positively related to amendment level.

Trend Analysis

Historical contaminant concentration data taken from groundwater wells in 1981, 1983, 1985, 1986, and 1991 (Dames and Moore, Inc. 1993) were analyzed for the following explosives and derivatives: 2,4DNT; 2,6DNT; DNB; octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); RDX; Tetryl; TNB; and TNT. Data sets were relatively complete for 1983, 1985, 1986, and 1991 for seven wells and the analytes TNB, TNT, 2,4DNT, and 2,6DNT (Table 1). Observations of the data showed that concentrations were decreasing in about 45 percent of the data sets for which concentrations exceeded detection limits (6 of 13 values). Analytes decreasing in concentrations were TNB (one data set), DNB (one data set), TNT (two data sets), 2,4DNT (one data set), and tetryl (one data set). These observations are spotty, rendering the data insufficient to define statistical trends in contaminant concentrations.

3 Groundwater Monitoring and Cone Penetrometer Sampling

Well Sampling Protocol

The initial monitoring plan was designed to sample 11 wells constructed at Site L1 during the RI investigations (Dames and Moore, Inc. 1993). The monitoring plan called for monthly sampling for 9 months. The wells were sounded to determine depth and to ensure that no obstructions were present. The measurements were also used to determine the length of tubing needed to sample each well. To prevent cross contamination, tubing of appropriate length was dedicated to each well, and existing analytical data were reviewed to establish a well-sampling order from least to greatest contaminant concentration. After recording a water level measurement, micropurge sampling techniques were employed to obtain formation water. Samples were collected using a 2-in. diameter low-flow pump for sampling wells as small as 2-in. in diameter. Field parameters were measured with an in-line Multi-Parameter Water Quality Monitor (Yellow Springs Instruments Company, Inc., Yellow springs, OH) with data transmitted directly to a laptop computer. Ecowatch software (1995, Yellow Springs Instruments, Yellow Springs, MO) was used to visualize in real-time the parameters being measured. The field data were recorded with time until formation water was obtained and sample collection proceeded. Formation water may be obtained by one of three options: (a) micropurge using a low-flow pump until a stable value for dissolved oxygen is obtained, (b) bailing a minimum of three well volumes, or (c) micropurge and bailing in combination. Field parameters monitored were dissolved oxygen (DO), temperature, salinity, pH, and conductivity.

Due to seasonally low water levels in the summer of 1997, three wells (MW171, MW175, and MW176) were dry. These wells were consequently dropped from the monitoring program. Three new wells (WES1, WES2, and WES3) were completed (July 1997) in the bedrock and integrated into the sampling plan. These wells were located to contribute to the vertical and northern definition of the contamination. The new wells were drilled to a depth

of 20 ft, which placed them into the Silurian age, dolomitic sandstone. The wells were 4 in. in diameter and completed with 20 ft of 10-slot polyvinyl chloride (PVC) screen. A standard sand filter pack was used to prevent the migration of fine silts and sands into the well-bore. After development by air lifting techniques, each well was tested for yield. Yields were approximately 5 gal per minute for WES1 and WES2 and approximately 8 gal per minute for WES3.

Cone Penetrometer Sample Collection

The objectives of the cone penetrometer (CPT) sampling were to refine available information on the geology of Site L1, delineate the contaminant plume, and collect soil samples for the biomarker research. Seven transects radiating from MW131 were sampled by CPT in June 1997 (Figure 3). The MW131 was selected as the center because it had exhibited the highest concentrations of TNT and RDX (Table 1). Three sites were sampled at multiple depth intervals to obtain a vertical profile of discrete samples. Each penetration was to bedrock. The first punch on a given transect was used to stratify the site by measuring resistivity to penetration. The strata were defined in terms of lithology, and the most advantageous sampling depth for microbial processes was selected. Subsequent punches were used to collect soil samples with a split spoon sampler (45.7 cm, or 18 in.) that had been sterilized to prevent contamination. Typically, at least three depths, surface, middepth, and just above bedrock, were sampled. Up to 400 g of soils were collected in the sampler. Samples were visually examined, logged, and placed in sterile bags for shipment to WES for analysis. Explosives and geochemical parameters (see below) were measured on these samples in addition to the biomarker research conducted with them.

Analytical Chemistry Methods and Analytes

Groundwater sample collection and preservation

Once formation water was achieved, three samples of groundwater were collected: a 1-L sample for explosives; a 500-ml sample for nitrate/nitrite, total organic carbon, total iron, calcium, magnesium, and manganese; and a 100-ml sample for sulfate and chloride. During the first and second sampling rounds, after collection of samples for the explosives and the geochemical parameters mentioned above, the wells were bailed for collection of zero headspace samples for methane determination. During sampling Round 3, a sample from each well was assayed for picric acid.

In order to increase confidence in observed trends in the data, results of two experiments conducted at the Louisiana Army Ammunition Plant (LAAP) under the Environmental Security Technology Certification Program were applied to the well sampling protocol for JAAP (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim

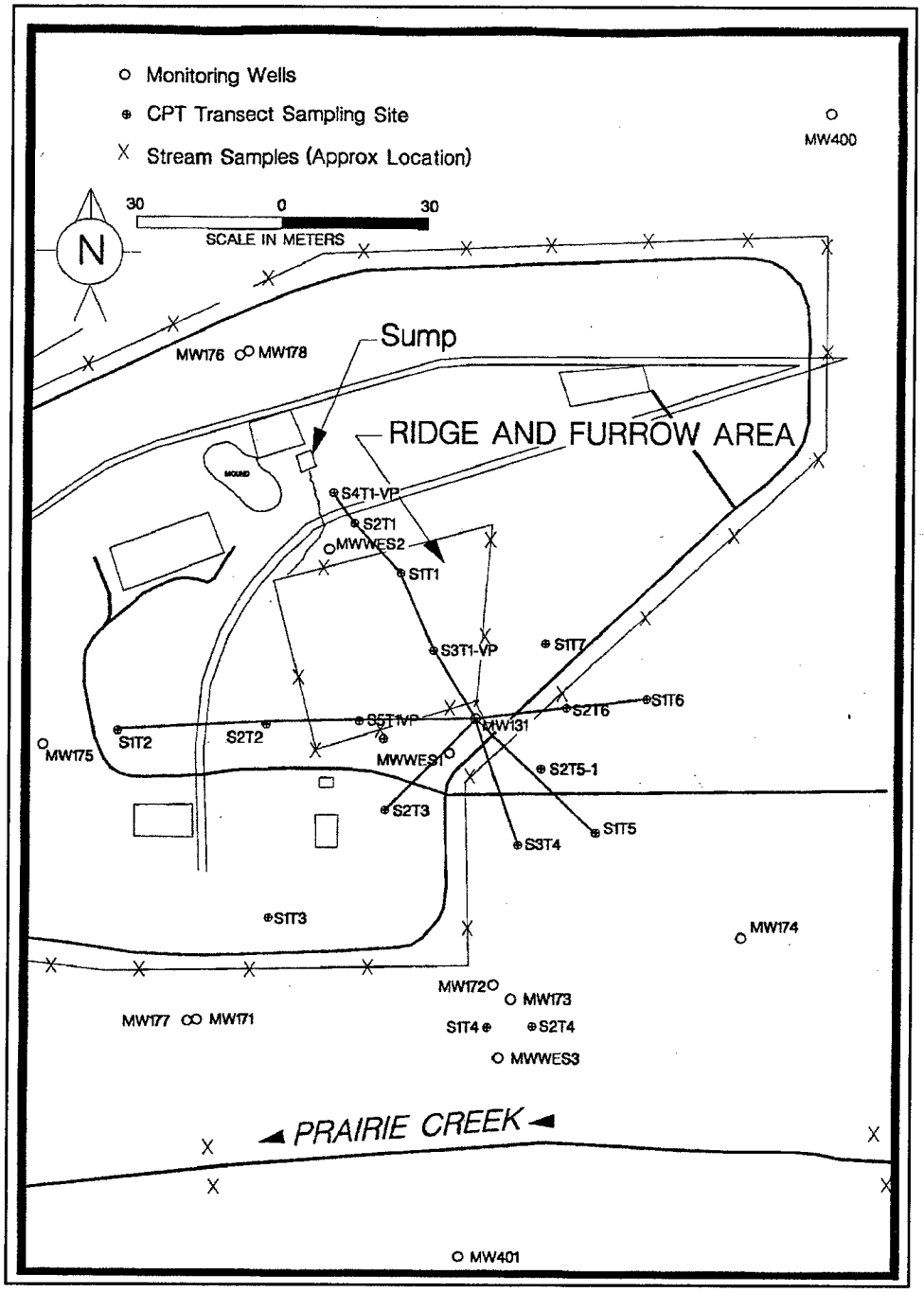

Figure 3. Location of monitoring wells and cone penetrometry sampling points at Site L1

Report"). Contributions to random error and systematic bias must be minimized to objectively determine whether observed trends in analyte concentrations are statistically significant. Results of experiments at LAAP confirmed that concentrations of explosives and their environmental transformation products change significantly as water is withdrawn from the wells. Concentrations stabilized, however, as concentrations of dissolved oxygen stabilized. Therefore, a criterion

was established whereby well water samples were collected after DO levels had been stable for 15 min of continuous low-flow pumping. When water elevations in wells were extremely low, bailing of three well volumes was used.

A second experiment assessed whether sample preservation was essential to prevent analyte loss during the period between sample collection and analysis (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"). Results indicated that chemical preservation was required to prevent losses of nitroaromatic explosives (particularly TNT and TNB) and that acidification to pH 2 was the most effective preservation technique evaluated. Therefore, a criterion was established by which all samples for explosives analyses were preserved by addition of sodium bisulfate to achieve a pH of 2.

Between wells, the sampling equipment was decontaminated by rinsing with distilled water three times. Rinsate from decontamination for at least one well each sampling day was analyzed for explosives as a check of the effectiveness of the decontamination procedure. To further minimize the effects of any carryover of contamination from one well to the next, wells were sampled in order from lowest to highest concentrations as defined by historical data and results of the first sampling round.

All monitoring wells, physical boundaries and features, and subsequent CPT and surface soil sampling locations were surveyed using a global positioning system.

Chemical analyses

Explosives and their products in groundwater. Judging from detections reported in the historical data for wells sampled at Site L1, the most significant explosives on the site are TNT, TNB, and RDX (Dames and Moore, Inc. 1993). Other detections included 2,6-dinitrotoluene, 2,4-dinitrotoluene, and 1,3-dinitrobenzene (Table 1). However, the presence of transformation products of these explosives provides evidence for initial subsurface processes that may prove relevant to natural attenuation mechanisms. Therefore, the list of explosives analytes was expanded to include additional transformation products.

The target analytes for EPA SW846 Method 8330 (EPA 1988) include the following: HMX, RDX, TNB, DNB, tetryl, TNT, nitrobenzene (NB), 4-amino-2,6-dinitrotoluene (4ADNT), 2-amino-4,6-dinitrotoluene (2ADNT), 2,4-DNT, 2,6-DNT, o-nitrotoluene (2NT), m-nitrotoluene (3NT), and p-nitrotoluene (4NT). All of these analytes except for the mononitrotoluenes were assayed. In addition to these analytes, several other compounds have been identified as potential environmental transformation products of TNT, RDX, and TNB. Those from TNT and TNB include 3,5-dinitroanaline (DNA), 2,4-diamino-6-nitrotoluene (2,4DANT), and 2,6-diamino-4-nitrotoluene (2,6DANT) and three isomeric azoxy compounds. All of these analytes were assayed except for the isomeric azoxy compounds. Standards were available for

only one of these, 2,2',6,6'-tetranitro- 4,4'-azoxytoluene (44'AZOXY). Therefore, only the 44'AZOXY isomer was assayed.

Samples were analyzed with and without a preconcentration step to broaden the range of detection from very low micrograms-per-liter to high micrograms-per-liter concentrations. Preconcentration was achieved by solid phase extraction. Analyte detection on the high performance liquid chromatography (HPLC) was achieved with an electron capture and an ultraviolet detector. Two columns having slightly different retention times for the analytes were run simultaneously to eliminate questionable peaks.

Three nitroso derivatives of RDX have been observed as microbial transformation products (McCormick, Cornell, and Kaplan 1981). They are hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX). All three of these analytes were assayed. Most of these compounds cannot be determined using Method 8330 as written. Therefore, a gradient elution RP-HPLC method was used. This method was designed to allow determination of compounds much more polar and much less polar than those on the Method 8330 target list.

Some explosives-contaminated sites contain picric acid, which was used during World War II in armor-piercing shells, bombs, and rocket warheads (Myers 1987). During one round of sampling (Round 1, May 1997), analysis for picric acid was performed with groundwater from MW131, the well exhibiting the highest explosives concentrations historically. Analytical results indicated the presence of picric acid; therefore, groundwater from all other wells was analyzed in Round 3, July 1997. When three new wells were installed, samples from them were also checked for picric acid (August 1997). Sample preparation for picric acid analysis was the same as for Method 8330. However, HPLC analysis used a mobile phase consisting of 40-percent methanol and 60-percent 0.5 M KH_2PO_4 buffer (pH adjusted to 3.5 with concentrated acetic acid). Elution was at 1.5 ml min^{-1} for 10 min. The Waters 586 Tunable Absorbance Detector (Waters Corp., Milford, MA) was set at 265 nm, which is maximum absorbance for picric acid.

Explosives and their products in soils. Soil samples were analyzed by Method 8330. The difference between the procedure for soils and water is the requirement of extracting the soil prior to injection into HPLC. Soils are extracted with acetonitrile using sonication. Analytical standards and analytes were the same as for analysis of groundwater sample.

Geochemical parameters in groundwater. Laboratory analyses included total iron, calcium, magnesium, and manganese (Method 6010, EPA 1988), total organic carbon (Method 505C, American Public Health Association 1985), nitrate-nitrite nitrogen (Method 353.2, EPA 1982), sulfate (Method 375.2, EPA 1982), and chloride (Method 325.2, EPA 1979). Samples for total iron, calcium, magnesium, and manganese, total organic carbon, and nitrate-nitrite nitrogen were preserved with 0.4 g $NaHSO_4$ to 250 ml of water. Samples for sulfate and chloride were not preserved. Iron speciation, Fe^{+2} and Fe^{+3}, was assayed in the

first two rounds of sampling (Round 1, May 1997, and Round 2, June 1997). Speciation was achieved by ion chromatographic separation (Dionex Corp., Sunnyvale, CA) of samples preserved with 1-percent HCl followed by analysis according to Method 6020 (EPA 1988) on a Perkin Elmer (Norwalk, CT) inductively coupled plasma mass spectrometer.

Samples for methane analysis were collected in Rounds 1 and 2 only by bailing the well after other samples had been collected by pumping. Samples were transferred from the bottom of the bailer into volatile organic analysis (VOA) tubes with silicon Teflon-faced septa using a volatile organic contaminant removal device to reduce contact between the sample and air. Samples were preserved with three drops of 1-percent HCl and stored at 4 °C for transport to the laboratory. Twenty-milliliter aliquots of well water were transferred by gas-tight syringe to 40-ml VOA tubes. The samples were allowed to equilibrate with the headspace. A standard curve was developed by adding four concentrations of standard (100-percent pure) nitrogen gas to similar 40-ml VOA tubes containing 20 ml of distilled water. Headspace of standards and samples were quantified on a Model 8610 gas chromatograph (SRI Instruments, Las Vegas, NE).

Geochemical parameters in soils. Soil samples were analyzed for pH, sulfate, nitrate nitrogen, nitrite nitrogen, phosphorus, total Kjeldahl nitrogen, and total organic carbon (TOC) (American Public Health Association 1985).

Round 10 well sampling

Due to unexpected elevations in concentrations of contaminants in the Round 9 data for MW131, an additional sampling of five wells was executed in March 1998. The wells included MW131, MW172, MW173, WES1, and WES2. Samples were split in the field with one sample being sent to the WES Environmental Chemistry Branch (ECB) as in previous rounds and the other being sent to a confirmation laboratory. The U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, served as the confirmation laboratory. Samples were analyzed by a direct injection HPLC method consistent with Method 8330. Direct injection, which results in higher detection limits, was used rather than preconcentration because high values were anticipated. The procedure employed different columns from those used by ECB as a further confirmation of results. The CRREL also analyzed split samples from Round 9 for MW131, MW172, MW173, and WES1.

Results

Explosives and their products in groundwater

Variability. The nine monthly sampling rounds exhibited limited variability for each analyte (Table 2), with three exceptions, Round 9 (January 1998) for

Table 2
Groundwater Concentrations ($\mu g\ L^{-1}$) of Explosives and Degradation Products for Site L1, Joliet Army Ammunition Plant

Well No.	Date	TNB	DNB	TNT	4ADNT	2ADNT	HMX	RDX	3,5DNA
MW131	05/17/97	1,420	0.2DL[1]	1,290	28.2	40.5	0.2DL	3.11	11.8
	06/12/97	2,000	2.79	1,740	39.8	57.1	0.2DL	3.78	10.6
	07/11/97	1,440	0.2DL	1,160	28.8	41.9	0.2DL	4.27	0.2DL
	08/09/97	1,930	1.86	1,540	36.7	55.2	0.2DL	4.10	7.7
	09/06/97	1,870	2.18	1,510	36.3	56.1	0.2DL	2.96	15.7
	10/02/97	1,910	2.17	1,580	38.2	57.6	0.2DL	2.80	6.8
	10/31/97	1,930	1.60	1,590	38.2	58.5	0.2DL	2.46	4.9
	12/02/97	1,920	1.81	1,630	38.5	62.5	0.2DL	2.62	5.6
	01/12/98	2,950	3.40	6,830	67.4	87.6	0.2DL	2.18	39.8
	03/17/98	3,630	7.02	12,130	91.8	93.3	0.2DL	3.59	89.7
MW172	05/16/97	2.13	0.2DL	9.09	2.58	1.99	0.40	5.01	0.32
	06/12/97	2.28	0.2DL	9.17	2.65	2.09	0.2DL	5.00	0.23
	07/10/97	2.01	0.2DL	8.56	2.53	2.00	0.2DL	4.65	0.2DL
	08/06/97	1.79	0.2DL	7.68	2.54	1.99	0.25	3.96	0.2DL
	09/05/97	1.99	0.2DL	8.49	2.81	2.19	0.31	4.11	0.32
	10/02/97	1.72	0.2DL	7.51	2.78	2.14	0.2DL	3.65	0.34
	10/30/97	1.79	0.2DL	8.05	2.88	2.20	0.2DL	3.77	0.45
	12/04/97	1.94	0.2DL	8.87	3.17	2.49	0.28	4.76	0.54
	01/15/98	1.85	0.2DL	7.92	2.59	2.14	0.29	4.18	0.52
	03/18/98	2.35	0.2DL	9.76	2.56	2.02	0.2DL	5.85	0.58
MW173	05/17/97	3.43	0.2DL	25.1	5.19	5.70	1.58	16.6	0.68
	06/12/97	4.57	0.2DL	31.4	5.09	5.78	1.71	19.4	0.44
	07/10/97	5.27	0.2DL	32.6	5.66	6.11	1.66	22.2	0.2DL
	08/07/97	5.44	0.2DL	34.6	6.53	7.07	1.85	22.0	0.32
	09/05/97	5.16	0.2DL	33.8	6.97	7.35	1.76	20.7	0.32
	10/02/97	4.80	0.2DL	33.2	7.10	7.33	1.78	21.1	0.53
	10/31/97	5.80	0.2DL	35.9	7.87	8.22	2.04	22.7	0.66
	12/05/97	4.76	0.2DL	32.8	6.86	7.32	2.17	22.7	0.71
	01/15/97	0.30	0.2DL	4.59	3.33	3.61	0.81	8.19	0.47

(Continued)

[1] Detection limit.
[2] J values are below the statistically reliable detection limits.

Table 2 (Concluded)

Well No.	Date	TNB	DNB	TNT	4ADNT	2ADNT	HMX	RDX	3,5DNA
MW173	03/18/98	3.28	0.2DL	19.1	4.41	4.63	1.24	12.8	0.61
WES1	08/07/97	12.2	0.2DL	12.2	4.69	6.27	0.2DL	0.63	4.31
	09/06/97	10.5	0.2DL	11.7	8.34	6.70	0.2DL	1.89	6.69
	10/02/97	12.7	0.21	16.5	11.5	8.37	0.2DL	0.26	8.80
	10/31/97	6.8	0.2DL	10.5	7.13	6.63	0.2DL	0.2DL	7.75
	12/05/97	2.4	0.2DL	4.7	3.80	4.12	0.2DL	0.41	4.09
	01/15/98	10.6	0.2DL	14.7	6.85	7.51	0.2DL	1.23	8.45
	03/18/98	30.1	0.13J[2]	35.6	12.3	13.5	0.2DL	0.58	15.7
WES3	08/07/97	0.99	0.2DL	1.69	0.87	0.84	0.2DL	1.30	0.21
	09/05/97	0.56	0.2DL	1.23	0.93	0.72	0.2DL	0.75	0.36
	10/01/97	0.56	0.2DL	1.07	0.88	0.67	0.2DL	0.68	0.38
	10/31/97	0.52	0.2DL	0.95	0.85	0.62	0.2DL	0.59	0.45
	12/04/97	0.53	0.2DL	0.93	0.75	0.63	0.2DL	0.67	0.41
	01/14/98	0.72	0.2DL	0.99	0.65	0.57	0.2DL	0.65	0.38

MW131 and MW173 and Round 8 (December 1997) for WES1. If the data from these exceptional rounds are omitted, the variability (standard deviation) for TNB, TNT, 4ADNT, and 2ADNT averaged 12-17 percent of the mean. Variability for RDX and DNA, both of which exhibit small means (<10 ppb), was higher.

Trends in 1997-1998 data. Only five wells exhibited explosives in all sampling rounds: MW131, MW172, and MW173 in nine sampling rounds and new wells WES1 and WES3 in all six sampling rounds (Table 2, Figure 4). Four other wells, MW174, MW177, MW401, and WES2, showed one to three low-level sporadic detections. The most highly contaminated wells were MW131, MW172, MW173, WES1, and WES3. Two wells, MW175 and MW400, never exhibited explosives. MW175 was not sampled after Round 4 due to insufficient water level. MW400 was sampled in Rounds 1 through 5, dropped because of no detectable explosives, and sampled again in Round 9 when no explosives were found. MW176 was not sampled because of low water level.

The following analytes were never detected: tetryl, NB, 2,6DNT, 2,4DANT, 2,6DANT, 44'AZOXY, MNX, DNX, and TNX. The following analytes were detected rarely: 2,4DNT and picric acid in MW131 only, HMX (MW172 and MW173), and DNB (MW131 and WES1). Concentrations of picric acid were 233 and 260 ppb in Rounds 1 and 3, respectively. A value of 81 ppb was reported for WES1. This value is below the statistically valid detection limit of 140 ppb; therefore, the value is considered unreliable. The most commonly detected analytes were as follows:

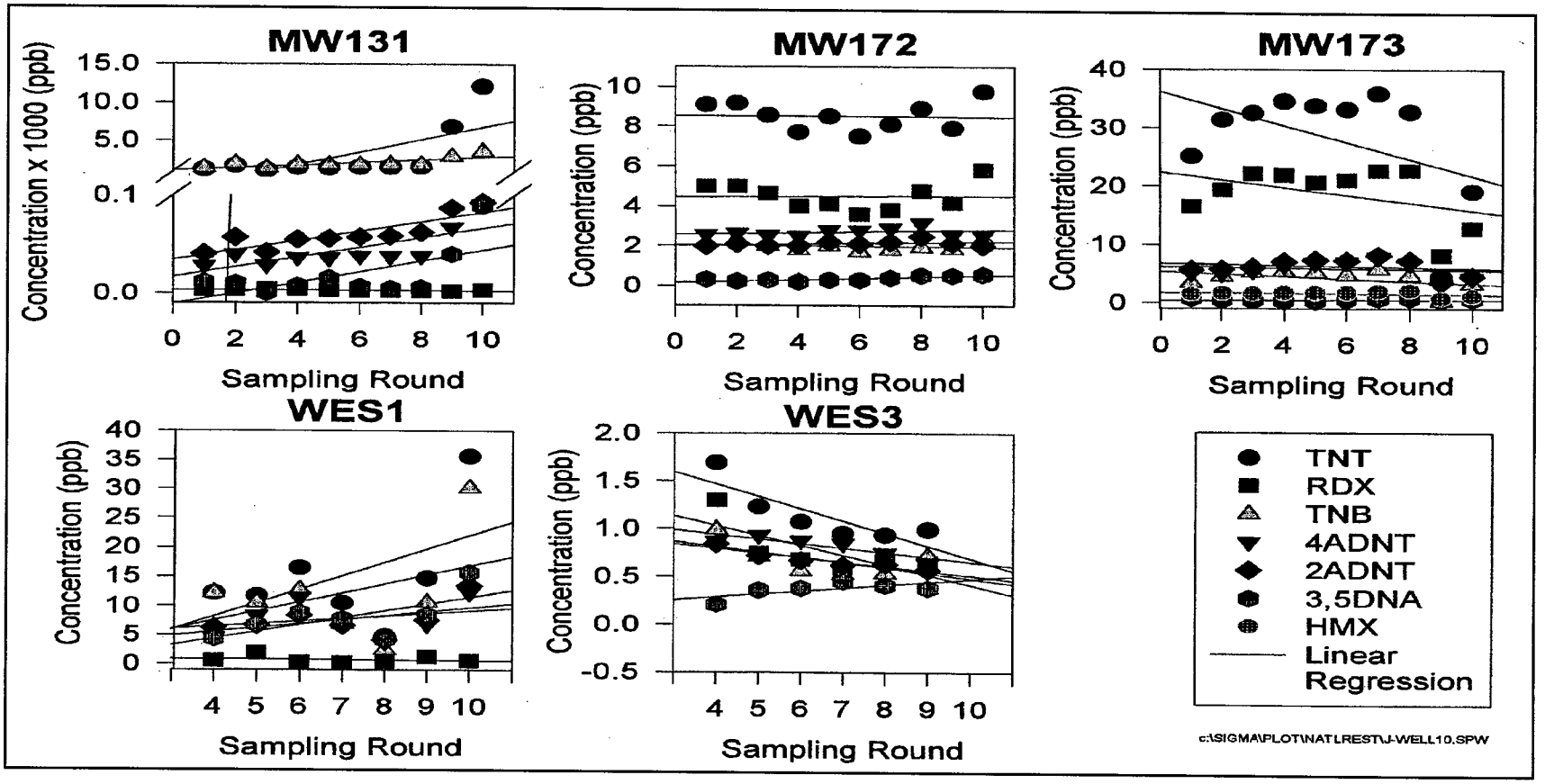

Figure 4. Results of 1997-1998 monitoring for the five wells exhibiting explosives in all sampling rounds (Monitoring well WES3 was not sampled in Round 10)

Analyte	Number of Detections	Number of Wells
RDX	44	8
TNB	40	6
TNT	40	6
2ADNT	39	5
4ADNT	39	5
DNA	35	5
HMX	14	2
DNB	8	2
2,4DNT	3	1
Picric acid	2	1

When the 1997-1998 data were regressed against time, data from only two wells exhibited linear regression coefficients greater than r^2 of 0.75, MW173 and WES2 (Table 3). In MW173, 4ADNT, 2ADNT, and HMX exhibited positive slopes of 0.36, 0.33, and 0.071 and r^2 values of 0.79, 0.79, and 0.85, respectively. In WES2, both 2ADNT and DNA exhibited a negative slope of -0.048 with r^2 values of 0.75 and 0.88, respectively. Except for the dramatic concentration increases observed for MW131 in Round 9, these results suggest that concentrations are changing too slowly to evaluate over a 9-month sampling period or that concentrations are no longer changing significantly at the site. Therefore, evaluating trends in concentration over time and changes in contaminant mass require data that have been compiled over at least several years.

Trends in all available groundwater data. Available historical data were combined with 1997 contaminant concentration data (omitting Round 9, January 1998) for trend analysis (Figure 5). Most analytes were below detection limits in most wells. Trend analysis was not attempted unless the data for a given well included at least two detectable concentrations. Trend analysis was performed using the SAS LIFEREG procedure (SAS Institute, Inc. 1988) assuming either a normal or a lognormal distribution. The LIFEREG procedure fits a regression line by maximum likelihood estimation (MLE) and is particularly well suited to analysis of censored data such as those with below detection limit observations. LIFEREG incorporates probabilities below detection limit for the assumed distribution and does not require prior reconstitution of the censored data (e.g., using one-half the detection limit). However, a simulation study in progress has shown the LIFEREG procedure to have a high Type I error rate[1] in some circumstances. Therefore, trend analysis was also performed by ordinary least squares (OLS) regression using linear, logarithmic, and quadratic models in the SAS REG procedure, following substitution of one-half detection limit for less than detection limit observations. Trends were not considered valid unless

[1] A Type I error is made by concluding no effect when an effect is real.

Table 3
Regression Statistics for Contaminant Concentration Trend Analyses, Rounds 1-8

Explosive	Well	MLE Regression Statistics[1]		OLS Regression Statistics[2]				Trend (Slope)
		X^2	P	Model	F	P	R^2	
2,6DNT	MW131	4.726	0.0297 *[3]	Linear	17.623	0.0018 *	0.638	-
2ADNT	MW131	11.021	0.0009 *	Linear	8.266	0.0282 *	0.579	+
	MW172	15.789	0.0001 *	Linear	11.842	0.0138 *	0.664	+
	MW173	31.382	0.0001 *	Linear	23.537	0.0028 *	0.797	+
	WES3	26.614	0.0001 *	Linear	15.969	0.0281 *	0.842	-
DNA	MW172	8.733	0.0031 *	Linear	6.550	0.0430 *	0.522	+
4ADNT	MW172	20.432	0.0001 *	Linear	15.324	0.0079 *	0.719	+
	MW173	30.279	0.0001 *	Linear	22.709	0.0031 *	0.791	+
	WES3	7.033	0.0080 *	Quadratic	19.577	0.0486 *	0.951	-
HMX	MW173	787.734	0.0001 *	Linear	612.682	0.0001 *	0.989	-
RDX	MW131	0.018	0.8933	Quadratic	105.335	0.0001 *	0.963	NS[4]
	MW172	32.566	0.0001 *	Linear	26.645	0.0006 *	0.748	-
	MW173	2.805	0.0940	Linear	2.295	0.1641	0.203	NS
	WES1	1.593	0.2069	Linear	0.961	0.3992	0.243	NS
	WES2	2.870	0.0902	Linear	1.722	0.2808	0.365	NS
	WES3	7.986	0.0047 *	Linear	4.792	0.1164	0.615	NS
TNB	MW131	10.385	0.0013 *	Linear	8.654	0.0147 *	0.464	+
	MW172	5.106	0.0238 *	Quadratic	5.019	0.0309 *	0.501	-
	MW173	0.297	0.5859	Linear	0.274	0.6108	0.024	NS
	WES1	13.422	0.0002 *	Linear	8.053	0.0658	0.729	NS
	WES3	17.769	0.0001 *	Linear	10.661	0.0469 *	0.780	-
TNT	MW131	0.998	0.3178	Linear	0.832	0.3832	0.077	NS
	MW172	7.929	0.0049 *	Linear	6.710	0.0251 *	0.379	-
	MW173	5.429	0.0198 *	Linear	4.594	0.0553	0.295	NS
	WES1	2.874	0.0900	Linear	1.724	0.2805	0.365	NS
	WES3	24.575	0.0001 *	Linear	14.745	0.0312 *	0.831	-

[1] Maximum likelihood estimate (MLE) regression statistic based on a normal distribution.
[2] Ordinary least squares regression statistic.
[3] * = Statistically significant, $\alpha = 0.05$.
[4] Trend not considered significant.

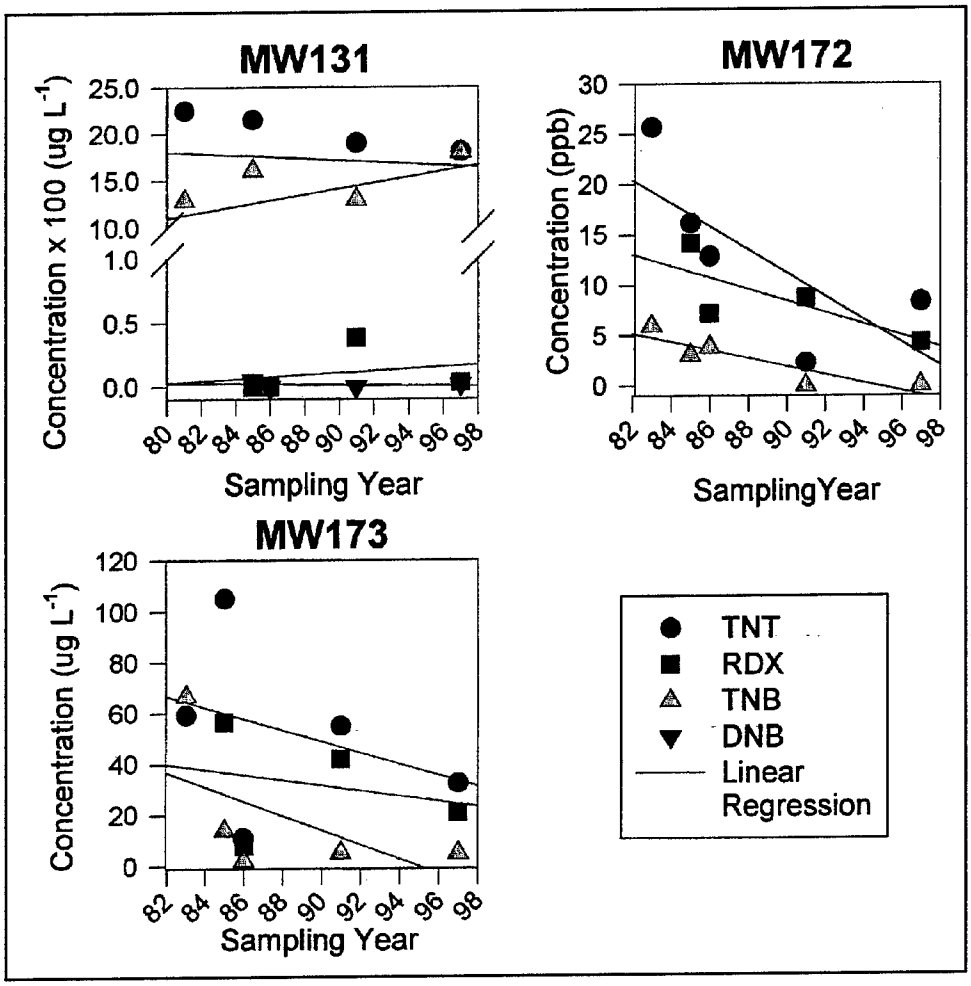

Figure 5. Historical and current explosives concentrations in the three wells exhibiting relatively complete data sets (The 1997 points are the mean of the first eight sampling rounds)

significant ($P < 0.05$) by at least one of the MLE models and one of the OLS models. Even so, the limited amount of data resulted in a number of trends that, while statistically significant, were undoubtedly influenced by outliers. Significant trends were observed for MW131, MW172, MW173, and WES3 (Table 4).

TNT concentrations were decreasing in two of the wells, MW173 and WES3. RDX was decreasing in MW172. RDX was decreasing in MW172. TNB was decreasing in MW173 and WES1, but increasing in MW131. Except for declines in WES3, significant trends for the TNT transformation products, 2ADNT, 4ADNT, and DNA, were increasing. The concentrations of 2,4DNT were increasing in MW131.

In general, the data are limited and highly variable (Table 5). Of the 216 statistical tests (12 wells x 18 analytes), only about 25 percent had values above

Table 4
Statistically Significant Trends in Contaminant Concentration Data from Joliet Army Ammunition Plant Wells, 1981-1997

Well	Contaminant	Trend	N	Remarks
MW131	2,6DNT	Decreasing	12	Increasing from 3 ppb in 1981 to 8 ppb in 1986, then dropping to <0.2 ppb from 1991 on
	2ADNT	Increasing	8	No historical data; generally increasing from 40 ppb in May 1997 to 63 ppb in Dec 1997
	TNB	Increasing	12	Wide range of concentrations from 755 to 2,000 ppb over the whole time period; considerable variability
MW172	2ADNT	Increasing	8	No historical data; 1997 concentrations all in the range from 2.0 to 2.5 ppb
	DNA	Increasing	8	No historical data; 1997 concentrations all in the range from 0.17 to 0.54 ppb
	4ADNT	Increasing	8	No historical data; 1997 concentrations all in the range from 2.53 to 3.17 ppb
	RDX	Decreasing	11	General decrease from 14 ppb in 1985 to 3-5 ppb in 1997
	TNB	Decreasing	13	Historical data highly variable; maximum 9.2 ppb in 1983, declining to <2 ppb in 1997
	TNT	Decreasing	13	Historical data highly variable; maximum 41 ppb in 1983, declining to 7-9 ppb in 1997
MW173	2ADNT	Increasing	8	No historical data; 1997 concentrations all in the range from 5.70 to 8.22 ppb
	4ADNT	Increasing	8	No historical data; 1997 concentrations all in the range from 5.09 to 7.87 ppb
	HMX	Decreasing	9	Only one historical data point, 44 ppb in 1991; 1997-98 concentrations 1-2 ppb
WES3	2ADNT	Decreasing	5	No historical data; slight decline from 0.84 ppb in Aug 1997 to 0.63 ppb in Dec 1997
	4ADNT	Decreasing	5	No historical data; slight increase initially, then decline from 0.93 ppb in Sep 1997 to 0.75 ppb in Dec 1997
	TNB	Decreasing	5	No historical data; slight decline from 0.99 ppb in Aug 1997 to 0.53 ppb in Dec 1997
	TNT	Decreasing	5	No historical data; slight decline from 1.69 ppb in Aug 1997 to <1 ppb in Dec 1997

detection limits. Of these, about 20 percent showed significant decreases in concentration over time, while about 11 percent showed increases; the remainder showed no trends. A closer examination of the results reveals that all of the increases occurred for transformation products of TNT, 2ADNT and 4ADNT, or for TNB and its transformation product DNA (Table 6). The number of wells exhibiting analyte decreases were small, but were in the relative order of decreasing analytes TNT=TNB>RDX=HMX=4ADNT=2ADNT=26DNT.

Table 5
Trend Summary: Number of Wells out of 12 Wells Sampled, Rounds 1-8

Contaminant	Wells with <3 Detectable Concentrations	Probable Trend		
		Not Significant	Decreasing	Increasing
2,4DANT	12			
2,4DNT	11	1		
2,6DANT	12			
2,6DNT	11		1	
2ADNT	7	1	1	3
DNA	7	4		1
44'AZOXY	12			
4ADNT	7	2	1	2
DNB	11	1		
DNX	12			
HMX	10	1	1	
MNX	12			
NB	12			
RDX	6	5	1	
Tetryl	12			
TNB	7	2	2	1
TNT	7	3	2	
TNX	12			

Round 9 anomalies and extra sampling (Round 10)

Concentrations of most detected analytes increased dramatically in MW131 in the Round 9 (January 1998) sampling (Table 2). Concentrations of TNT increased by a factor of six over previous rounds. Concentrations of 3,5DNA increased by a factor of eight; concentrations of TNB, 4ADNT, and DNB increased by a factor of two; and concentrations of 2ADNT increased by nearly a factor of two. RDX remained within the previous range. Concentrations of TNT, 3,5DNA, 4ADNT, 2ADNT, HMX, and TNB in MW173 dropped significantly.

Results from a follow-up additional sampling (March 1998) of MW131, MW172, MW173, WES1, and WES2 revealed even higher contaminant concentrations in MW131 (Table 2). The concentration of TNT was twice that of Round 9. Concentrations in MW173 had increased, but remained lower than

Table 6
Concentrations of Geochemical Parameters in Groundwater (mg L^{-1})

Well No.	Date	Calcium	Magnesium	Manganese	Total Iron	Nitrate/Nitrite Nitrogen	Sulfate	Chloride
MW131	05/17/97	108	47.7	0.058	0.195	4.58	53.6	5.28
	06/12/97	104	44.6	0.018	<0.02	4.91	48.9	4.74
	07/11/97	99.9	45.7	0.012	<0.02	9.06	64.2	4.82
	08/09/97	125	50.5	0.027	<0.02	7.93	34.7	2.49
	09/06/97	165	60.8	0.071	0.033	8.54	5.18	<0.38
	10/02/97	135	62.9	0.133	0.123	24.9	3.92	<0.38
	10/31/97	155	79.6	1.02	2.05	26.6	118	6.94
	12/02/97	161	68	0.467	0.823	6.01	108	9.67
	01/12/98	127	49.2	0.03	0.081	5.81	62.5	2.9
	03/17/98	84.3	26.9	0.291	0.226	14.8	36.3	1.24
MW172	05/16/97	94.6	45.1	<0.001	0.026	3.15	62.4	11.4
	06/12/97	93	44.2	<0.001	<0.02	3.54	57.5	10.8
	07/10/97	90.9	45.4	<0.001	<0.02	4.08	62.2	11.1
	08/06/97	101	44.8	<0.001	<0.02	4.37	30.6	5.8
	09/05/97	117	44.6	<0.001	<0.02	4.02	2.95	0.435
	10/02/97	93.8	47.8	<0.001	<0.02	3.72	2.49	0.391
	10/30/97	96.8	47.8	<0.001	0.045	8.09	73.5	9.06
	12/04/97	106	47.5	<0.001	<0.02	2.94	68.7	8.82
	01/15/98	105	48.1	<0.001	<0.02	2.45	70.3	7.72
	03/18/98	103	48.6	<0.001	<0.02	3.32	56.2	13.6
MW173	05/17/97	130	59.6	0.004	<0.02	2.37	191	6.83
	06/12/97	101	47.8	0.002	<0.02	2.5	86.8	7.11
	07/10/97	96.5	44.1	0.006	0.058	2.16	79.2	8
	08/07/97	91.6	44.3	<0.001	<0.02	2.61	29.1	3.61
	09/05/97	107	42.8	<0.001	<0.02	2.82	2.91	<0.38
	10/02/97	95.8	46.3	0.003	<0.02	2.3	0.522	<0.38
	10/31/97	89.8	45.4	0.022	0.134	3.06	65.1	7.23
	12/05/97	105	46.7	0.009	0.021	2.39	66.4	7.84
	01/15/98	401	214	0.022	0.049	1.65	1,433	15.8

(Sheet 1 of 3)

[1] NS = Not assayed.

Table 6 (Continued)

Well No.	Date	Calcium	Magnesium	Manganese	Total Iron	Nitrate/Nitrite Nitrogen	Sulfate	Chloride
	03/18/98	131	65.4	0.004	0.027	4.24	226	8.70
MW174	05/16/97	89.03	42	0.002	0.026	<0.02	54.5	8.93
	06/11/97	92.24	39.9	<0.001	<0.025	<0.02	51.2	9.84
	07/09/97	83.3	NS[1]	<0.001	0.026	<0.02	58.1	8.34
	08/06/97	89.6	41.8	<0.001	0.025	<0.02	27.1	4.41
	09/04/97	113	39.7	<0.001	0.052	<0.02	3.04	0.512
	10/01/97	97	44.6	0.001	0.036	0.177	2.7	0.742
	10/29/97	96.1	47.2	0.004	0.03	0.262	83.1	27.8
	12/03/97	108	48.3	0.009	0.04	0.025	7.8	6.12
	01/13/98	113	47	0.005	0.021	<0.02	89.9	38.9
MW175	05/15/97	75.2	33.8	<0.001	<0.02	0.28	43.9	1.16
	06/11/97	83.56	35.7	0.021	0.492	0.359	44.6	1.45
	07/09/97	128	NS	0.313	3.02	0.25	46.7	0.832
MW177	05/15/97	93.6	46.0	0.033	<0.02	0.13	79.3	3.34
	06/11/97	96.76	46.4	0.062	<0.02	0.132	89.6	3.51
	07/09/97	87.7	NS	0.066	<0.02	0.112	89.4	3.31
	08/05/97	92.9	46.0	0.088	<0.02	0.081	43.3	1.86
	09/04/97	117	48.2	0.110	<0.02	0.074	4.2	<0.375
	09/30/97	96.3	47.1	0.063	<0.02	0.051	3.22	<0.375
	10/29/97	96.2	50.0	0.062	<0.02	0.051	92.4	3.69
	12/03/97	95.5	46.4	0.064	<0.02	0.075	75.4	29.6
	01/13/98	96.1	45.1	0.026	<0.02	0.126	85.5	3.56
MW178	05/15/97	97.1	47.6	<0.001	<0.02	3.49	48.1	7.7
	06/11/97	100.3	48	<0.001	<0.02	3.75	55.8	7.88
	07/09/97	96.2	NS	<0.001	<0.02	4.68	62.3	9.31
	08/05/97	103.0	47.2	0.002	<0.02	5.4	30.2	5.35
	09/04/97	112.0	47.3	<0.001	0.021	5.63	3.04	0.478
	09/30/97	89.1	48.9	<0.001	<0.02	7.98	2.5	0.483
	10/28/97	89.8	49.5	<0.001	<0.02	8.83	69.4	13.5
	12/02/97	91.0	49.1	<0.001	<0.02	4.32	64.3	11.5
	01/13/98	102.0	49.7	<0.001	<0.02	3.78	61	8.87

(Sheet 2 of 3)

Table 6 (Concluded)

Well No.	Date	Calcium	Magnesium	Manganese	Total Iron	Nitrate/Nitrite Nitrogen	Sulfate	Chloride
MW400	05/14/97	111	52	0.218	0.754	1.05	97.3	21.9
	06/10/97	109.9	51.1	0.277	0.755	<0.02	102	22.7
	07/08/97	106	NS	0.244	1.02	<0.02	105	22.2
	08/06/97	107	52.2	0.246	1.27	<0.02	51.2	10.9
	09/04/97	102	49.5	0.239	1.22	<0.02	5.31	0.93
	01/12/98	114	51	0.213	1.13	<0.02	108	22.3
MW401	05/16/97	110	53.1	0.027	1.49	<0.02	68.2	50.1
	06/11/97	109.2	52.9	0.025	1.61	<0.02	71.4	42.3
	07/09/97	102	51.6	0.023	1.51	<0.02	78.2	31.2
	08/06/97	110	49.4	0.024	1.77	<0.02	38.5	16
	09/05/97	128	48.3	0.024	1.78	<0.02	3.91	1.24
	10/01/97	99.2	52.2	0.033	1.57	0.263	3.14	1.17
	10/29/97	98.4	51.4	0.032	1.52	0.067	86.8	25
	12/03/97	110	51.9	0.038	1.31	<0.02	71.1	18.2
	01/14/98	110	52	0.027	1.6	<0.02	75.2	38.6
WES1	08/07/97	97.2	46.4	0.04	<0.02	5.19	35.6	4.17
	09/06/97	112	46.5	0.036	0.023	5.08	3.55	<0.38
	10/02/97	102	48.3	0.056	0.022	5.22	0.479	<0.38
	10/31/97	96.7	48.4	0.033	0.024	4.58	77.3	6.87
	12/05/97	101	46	0.013	<0.02	3.38	73.3	7.46
	01/15/98	96.7	43	0.017	<0.02	4.2	69.3	17.7
	03/18/98	80.4	37.2	0.021	0.026	0.272	47.7	6.50
WES2	08/07/97	98.6	47.2	0.004	<0.02	2.61	33.1	2.75
	09/05/97	119	46.7	0.002	0.032	3.07	3.26	<0.38
	10/01/97	98.5	49.9	0.001	0.054	2.83	2.6	<0.38
	10/30/97	99.9	50.7	<0.001	0.024	3.38	72.4	5.59
	12/04/97	98.4	50.8	0.002	<0.02	1.6	31.1	3.42
	01/14/98	105	49.2	0.019	0.019	3.85	71.1	20.9
	03/17/98	86.1	43.3	0.004	<0.02	0.749	48.3	3.18
WES3	08/07/97	108	48.4	<0.001	<0.20	3.29	36.1	3.92
	09/05/97	122	47.7	<0.001	<0.20	2.88	3.93	<0.38
	10/01/97	95.2	52.4	<0.001	<0.20	4.68	3.18	<0.38
	10/30/97	103	53	<0.001	<0.20	2.65	90.3	6.71
	12/04/97	111	51.2	0.002	<0.20	1.93	71	18.5
	01/14/98	107	50.2	0.001	<0.20	1.73	92.4	6.38

(Sheet 3 of 3)

observed in Rounds 1-8. Round 10 samples also showed the appearance of several analytes not observed above detection limits in the first nine rounds: 2,6DANT in MW131 (9.55 $\mu g\ L^{-1}$) and in WES2 (6.67 $\mu g\ L^{-1}$); 2,4DANT in MW131 (4.01 $\mu g\ L^{-1}$) and in WES2 (5.27 $\mu g\ L^{-1}$); and 2,4DNT in WES2 (0.52 $\mu g\ L^{-1}$).

Results from the confirmation laboratory for Round 9 (MW131, MW172, MW173, and WES1) and Round 10 (MW131, MW172, MW173, WES1, and WES2) were within 10 percent of values determined by ECB.

Geochemical parameters in groundwater

General groundwater quality. Concentrations of calcium and magnesium suggest that JAAP groundwater is rather hard and may require softening (when >200 mg L^{-1}) if ever put to household use (Table 6). Manganese concentrations were generally low, but several values (MW131, MW177, MW400, and WES1) were in exceedance of the drinking water regulatory limit of 0.05 mg L^{-1}. Four wells (MW131, MW175, MW400, and MW401) exhibited total iron concentrations above the drinking water standard of 0.3 mg L^{-1}. Values for all wells ranged from less than the detection limit of 0.02 to 1.78 mg L^{-1} (MW401). Nitrate/nitrite nitrogen values were generally low. The range for natural waters is 0.1 to 10 mg L^{-1} (Driscoll 1986). Most values were much less than 10 mg L^{-1}. Values in the range of 20 to 90 mg L^{-1} in drinking water are considered harmful to infants. Values for two samples taken from MW131 fell within the lower end of this limit; 24.9 and 26.6 mg L^{-1} were collected on 10/02/97 and 10/31/97, respectively. Sulfate concentrations were relatively low. Most values were less than 100 mg L^{-1}. Chloride concentrations less than 150 mg L^{-1} are considered satisfactory for most purposes. Chloride concentrations were only slightly higher than this value. No methane or reduced iron was observed.

Correlations with explosives data. Contaminant concentration data were analyzed with concurrent geochemical parameter measurements (Ca, Fe, Mg, Mn, TOC, NO_2/NO_3, SO_4, and Cl) and water levels to determine whether contaminants were correlated with any of these parameters (Table 7). Both Pearson's *r* and Spearman's nonparametric correlation analyses were conducted, because of the large number of less than detection limit values for explosives. Correlations were considered significant only when both analyses produced significant results ($P < 0.05$). Most of the significant correlations occurred in MW173, and all of those (correlations with Ca, Mg, TOC, SO_4, and water level) were negative. More explosives data correlated with TOC than with any other parameter. However, these results, taken as a whole, indicate no consistent influence of geochemical characteristics on explosives concentrations.

Table 7
Significant Correlations ($P < 0.05$ for Both Pearson's r and Spearman's Rho) Between Geochemical Parameters and Contaminant Concentrations, Rounds 1-8

Geochemical Parameter	Significant Positive Correlations (r, P, n)		Significant Negative Correlations (r, P, n)	
	Contaminant(s)	Well	Contaminant(s)	Well
Ca	--	--	RDX (-0.758, 0.0292, 8)	MW131
			TNB (-0.902, 0.0022, 8)	MW173
Fe	--	--	--	--
Mg	DNA (0.769, 0.0256, 8)	MW172	RDX (-0.840, 0.0090, 8)	MW131
	DNA (0.893, 0.0413, 5)	WES1	TNB (-0.894, 0.0028, 8)	MW173
Mn	TNB (0.919, 0.0273, 5) TNT (0.998, 0.0001, 5)	WES1	--	--
TOC	2ADNT (0.902, 0.0022, 8)	MW131	HMX (-0.719, 0.0445, 8) TNT (-0.740, 0.0359, 8) 4ADNT (-0.913, 0.0015, 8) 2ADNT (-0.923, 0.0011, 8)	MW173
NO_2/NO_3	TNB (0.972, 0.0056, 5) TNT (0.918, 0.0277, 5)	WES1	--	--
SO_4	--	--	TNT (-0.834, 0.0100, 8)	MW173
Cl	RDX (0.722, 0.0430, 8)	MW172	4ADNT (-0.963, 0.0083, 5)	WES3
Water level	RDX (0.835, 0.0100, 8) TNB (0.853, 0.0071, 8) TNT (0.789, 0.0200, 8)	MW172	2ADNT (-0.728, 0.0406, 5)	MW131
			TNB (-0.873, 0.0046, 8) TNT (-0.896, 0.0026, 8)	MW173

Geochemical parameters in soils

Soil pH was generally slightly alkaline. Results for other analytes indicated sufficient nutrients, specifically nitrogen, phosphorus, and organic carbon, to support abundant microbial activity at most depths (Table 8).

Stratigraphy as determined by cone penetrometer sampling

Results of cone penetrometer lithologies indicated a persistent clay layer of glacial origins underlying most of Site L1 (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"). Typically, the clay was first encountered at 1.5 to 2.5 ft below ground level and was 5 to 10 ft thick (Figures 6, 7, and 8).

The hydraulic gradients varied from 0.03 for the glacial materials to 0.0007 for the bedrock. The water levels in the updip areas of the site were about 1 m higher than those near Prairie Creek, thereby suggesting a downward flow into

Table 8
Concentrations of Geochemical Parameters in CPT Soil Samples (mg kg^{-1})

Sample	Soil pH	Sulfate	Nitrate Nitrogen	Nitrite Nitrogen	Phosphorus	TKN	TOC
S1-T1-2-10[1]	8.2	11	4	2	314	15.2	8,880
S1-T1-3-15	7.9	18	3	2	281	<3.66	10,600
S1-T1-4-15.5	7.8	182	1	1	311	<4.51	9,830
S1-T1-5-17.1	7.8	174	2	1	257	<9.43	9,480
S1-T3-2-2	6.3	38	3	2	396	63.1	5,960
S1-T2-2-5.1	8.1	16	4	1	270	15	6,560
S1-T2-3A-11	7.8	513	1	2	312	<9.60	11,500
S1-T2-4A-13	8.1	17	3	2	208	<11.9	6,240
S1-T2-5A-14.8	8	53	1	1	257	39.3	8,160
S1-T3-3-6.1	8.1	25	4	2	325	<11.9	8,310
S1-T3-4-9.8	8.1	16	3	1	280	<10.1	4,910
S1-T4-3A-4.8	7.5	477	4	2	306	27.4	6,100
S1-T4-4B-7.1	7.2	615	Not Run[3]	1	259	31	8,130
S1-T4-4C-7.1	7.3	282	3	1	504	41.3	6,050
S1-T5-2-6.1	8.3	10	3	2	303	16.5	6,420
S1-T5-3-8.5	8.1	58	1	2	251	<8.27	6,990
S1-T5-4A-12.5	7.7	632	1	2	294	55.6	15,100
S1-T6-2-5.9	8.2	10	3	1	325	11.6	7,570
S1-T6-3-12.5	8.2	15	2	1	295	19.7	5,390
S1-T6-3B-10	8.1	13	4	1	264	12.3	8,820
S1-T6-4-23	8.1	24	4	1	190	<10.3	9,180
S1-T7-2-SURFACE	7.7	6	5	1	370	76.3	9,340
S1-T7-3-3	8.1	15	3	2	297	17.3	5,480
S1-T7-4-7.1	8.1	10	4	1	334	<11.4	6,910
S1-T7-5-18.5	8.1	14	2	1	227	23.8	9,230
S2-T1-2-3	8.1	13	3	1	316	11	9,020
S2-T1-3-16.1	8.3	10	3	1	323	19.6	9,430
S2-T1-4-20.5	7.8	214	3	1	243	<11.3	11,600
S2-T1-5A-0	7.2	26	3	1	370	29.2	12,100

(Continued)

[1] Last two numbers are depth from surface in feet.
[2] Quantity of sample insufficient.
[3] Two samples were combined from this depth.

Table 8 (Concluded)

Sample	Soil pH	Sulfate	Nitrate Nitrogen	Nitrite Nitrogen	Phosphorus	TKN	TOC
S2-T2-2-2-3.6	8.1	13	1	1	330	<11.5	8,380
S2-T2-3-8	8.2	11	4	1	328	<11.0	9,400
S2-T2-4-14.6	8.1	7	3	1	313	<11.7	8,460
S2-T3-2-2	7.9	11	2	1	326	12	9,300
S2-T3-3-5.1	8.3	10	4	1	318	<10.2	9,040
S2-T3-4-8.4	8.2	10	1	1	261	<10.8	6,680
S2-T4-2-SURFACE	7.3	17	5	1	527	158	25,700
S2-T4-3&3A-3.3[3]	7.6	96	3	1	327	43.4	12,500
S2-T4-4A&4C-5.7[3]	8.1	44	3	2	185	12.7	3,940
S2-T5-2-2.5	8.1	10	4	1	391	23.3	8,700
S2-T5-3-7.5	8.3	10	4	2	232	24.3	3,690
S2-T5-4-10.5	8	5	4	2	230	<10.2	6,010
S2-T5-5-SURFACE	7.1	5	4	1	345	44.7	9,400
S2-T6-2-3.9	6.3	10	3	1	442	<12.4	2,140
S2-T6-3-9.5	8	13	4	1	492	<10.9	7,360
S2-T6-4-14.1	7.6	9	3	1	281	<10.5	9,050
S3-T1-2-SURFACE	7.9	8	1	1	361	87.8	14,500
S3-T1--3-5.5	8	13	3	1	330	13.5	7,500
S3-T1-4-13.5	8	10	1	1	239	<10.6	3,660
S3-T4-2-0.5	7.8	7	4	1	217	23.6	9,890
S3-T4-5A-2	7.3	9	1	1	559	90.6	11,200
S3-T4-3A&3B-9[3]	8	7	3	2	409	18.9	5,670
S3-T4-4B&4C-11.5[3]	8	32	2	1	203	<11.5	9,780
S4-T1-3-5.1	8	12	4	1	331	15.8	9,260
S4-T1-4-9.5	7.9	17	3	1	314	<11.1	8,540
S4-T1-5-17.6	7.4	247	3	1	355	36.4	13,200
S4-T1-6-2	6.6	13	1	2	287	26.2	4,490

the bedrock. Water levels from wells completed near Prairie Creek suggested little downward movement and indicated that groundwater flows horizontally along permeable zones until discharged into Prairie Creek. These observations are consistent with flow direction reported previously (Dames and Moore, Inc. 1993).

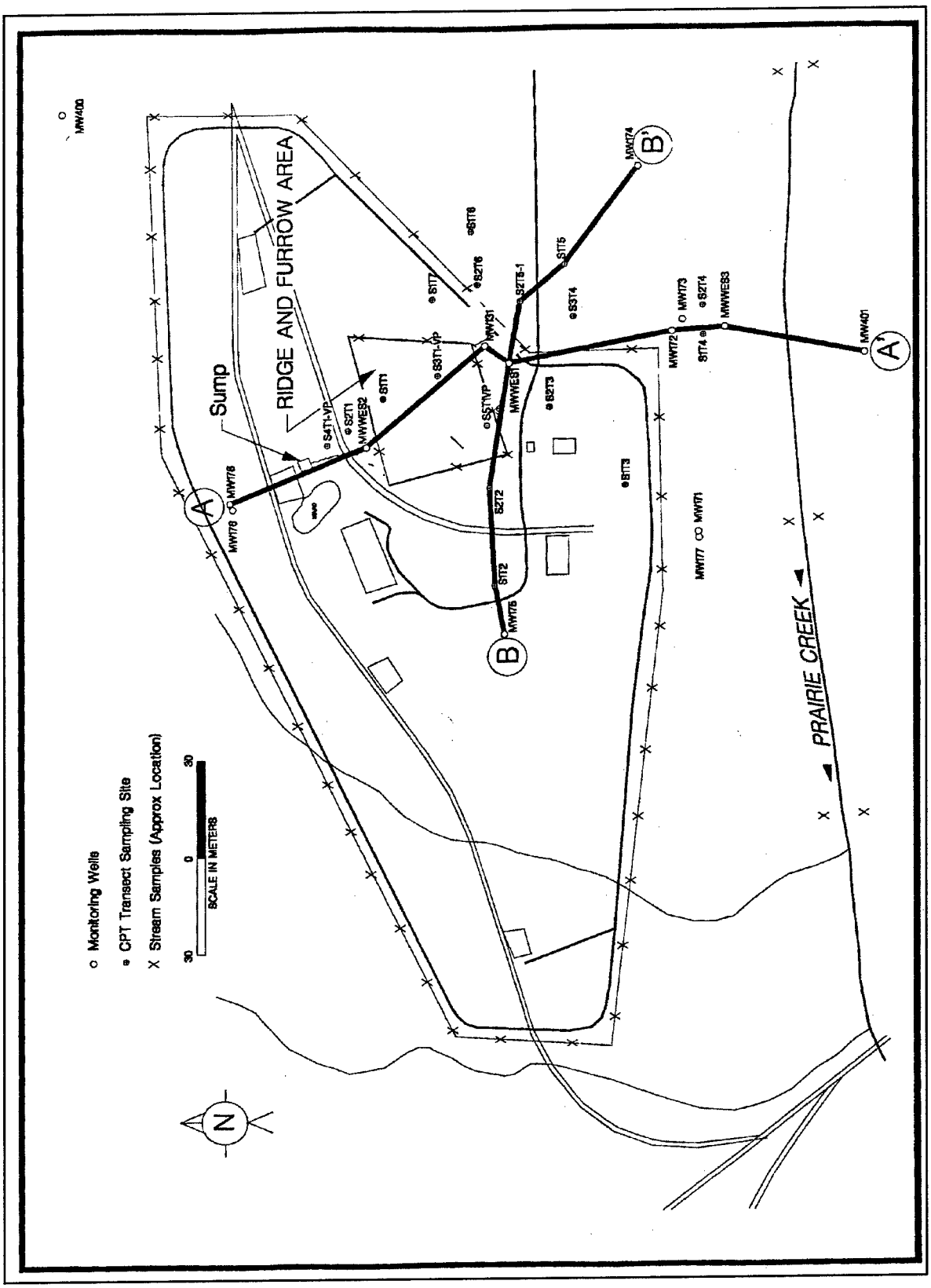

Figure 6. Locations of cross section A-A′ and B-B′ at Site L1

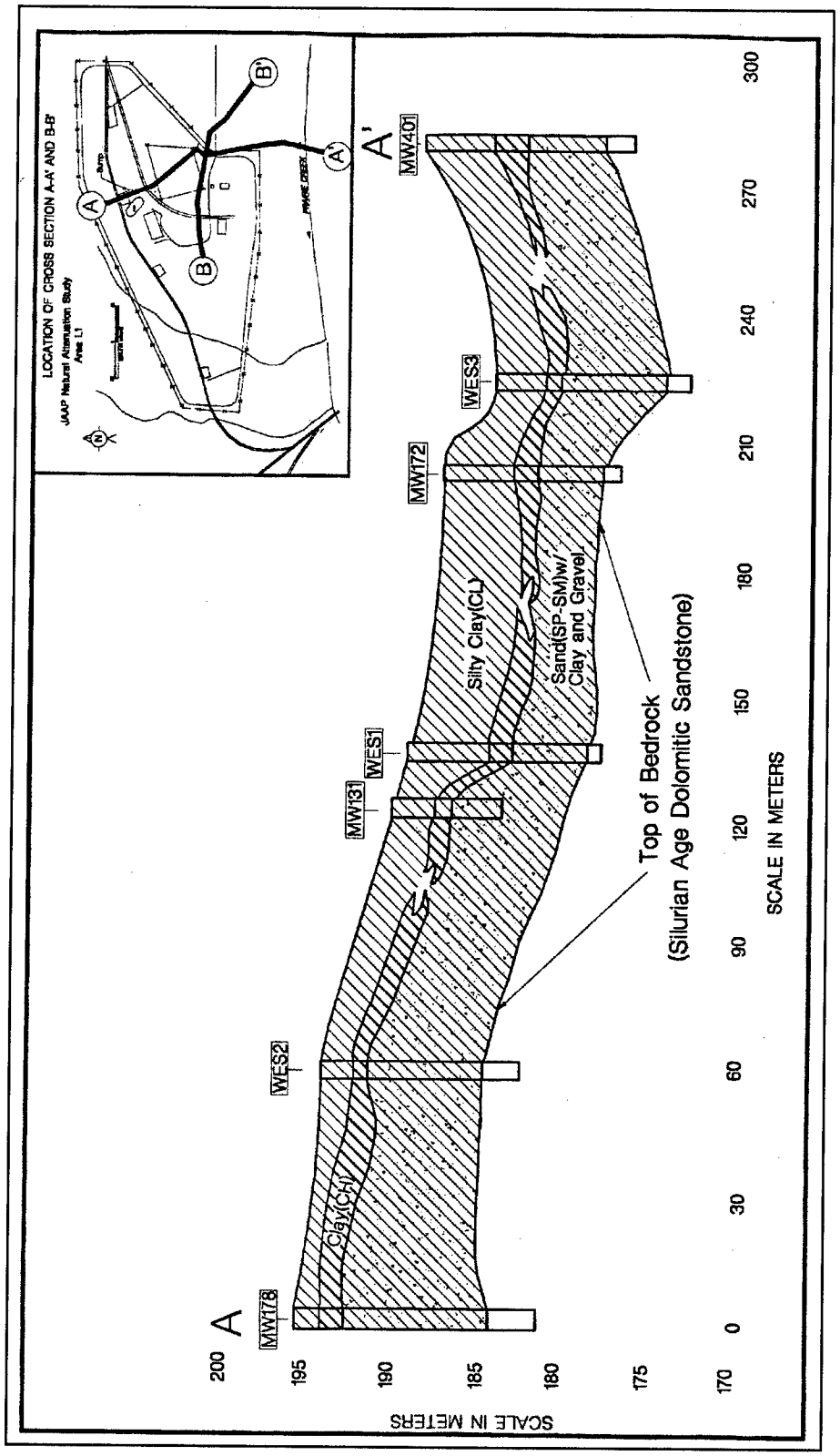

Figure 7. Cross section A-A' illustrating general north to south subsurface lithology

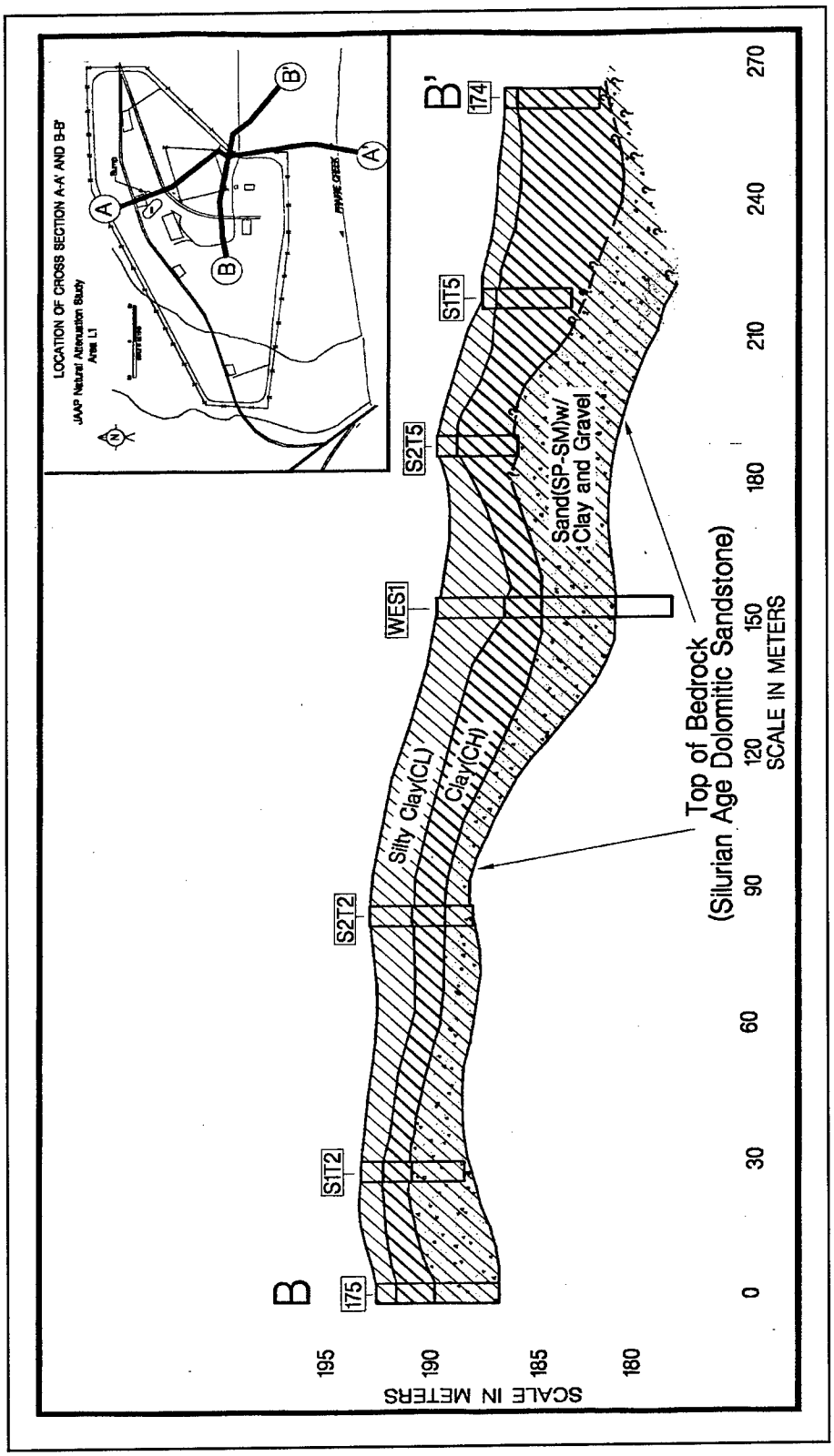

Figure 8. Cross section B-B′ illustrating general east to west subsurface lithology

Contaminant concentrations in cone penetrometer samples

Analyses of soil samples collected at sites along the transects indicated that most of the contamination was concentrated on top of the clay layer and was restricted to the ridge and furrow system (Table 9). Only 7 of the 56 samples showed concentrations above detection limits. Five of these were on Transect 1, which passes through the ridge and furrow system. The other two were along Transect 4. The highest concentration was for TNT (2.39 mg kg^{-1}). However, much higher concentrations were detected in surface soil samples collected in the ridge and furrow system (see Chapter 4). The contamination was very heterogeneously distributed over the ridge and furrow system.

Table 9
Explosives in CPT Soil Samples (mg kg^{-1})[1]

Sample	RDX	TNB	TNT	4ADNT	2ADNT	24DNT	4,4AZOX	35DNA
S1-T1-2-10	0.047J[2]	0.796	0.072J	0.208	0.353	0.028J	5.00DL[3]	0.158
S1-T1-3-15	0.167	0.2DL	0.2DL	0.2DL	0.2DL	0.2DL	5.00DL	0.069
S1-T1-4-15.5	0.148	0.042J	0.055J	0.073J	0.2DL	0.2DL	5.00DL	0.074J
S1-T1-5-17.1	0.2DL	0.019	0.2DL	0.2DL	0.2DL	0.2DL	5.00DL	0.014J
S2-T2-4-14.6	0.2DL	0.2DL	0.2DL	0.2DL	0.2DL	0.2DL	5.00DL	0.031J
S2-T4-2-SURFACE	0.2DL	0.2DL	0.2DL	0.043	0.022	0.2DL	5.00DL	0.2DL
S3-T1-2-SURFACE	0.2DL	0.251	0.991	0.9	1.13	0.219	0.105J	0.126
S3-T1-3-5.5	0.2DL	0.2DL	0.2DL	0.061J	0.071J	0.2DL	5.00DL	0.2DL
S3-T1-4-13.5	0.2DL	0.2DL	0.2DL	0.2DL	0.02J	0.2DL	5.00DL	0.2DL
S3-T4-3A&3B-9[4]	0.2DL	0.2DL	0.2DL	0.017J	0.2DL	0.2DL	5.00DL	0.2DL
S3-T4-4B&4C-11.5[4]	0.464	0.964	2.39	0.442	0.484	0.2DL	5.00DL	0.2DL
S4-T1-2-SURFACE	0.2DL	0.2DL	0.2DL	0.013J	0.2DL	0.2DL	5.00DL	0.2DL

[1] Only samples having at least one analyte above detection limits are presented.
[2] J values are below the statistically reliable detection limits
[3] Detection limit.
[4] Two samples were combined from this depth.

4 Biomarkers

Lines of Evidence

The evaluation and implementation of natural attenuation must follow lines of evidence that have been tailored specifically to explosives-contaminated sites. These lines of evidence are as follow (EPA 1997):

a. Document declining contaminant concentrations and/or changes in contaminant distribution at the field scale. This line of evidence focuses on an examination of available data for the site to determine possible decreases in contaminant concentration and distribution. The review of data must determine whether the concentrations of contaminants are increasing or decreasing due to physical, chemical, or hydrologic mechanisms.

b. Define mechanisms responsible for natural attenuation and determine if the rate at which such mechanisms can achieve remedial goals. This line of evidence mandates a search for and identification of potential biological, chemical, or physical markers providing indications that contaminants are being attenuated at the site.

c. Show the effectiveness of natural attenuation mechanisms. This line of evidence depends upon the collection of evidence demonstrating that natural attenuation onsite will provide adequate protection of human health and the environment. This evidence will be collected through monitoring.

While the first line of evidence can largely be obtained from existing historical information supplemented with a monitoring plan, obtaining data for the second and third lines of evidence will require site-specific sampling and analyses. Modern molecular microbiological tools (biomarkers) offer rapid, accurate, and sensitive means for determining in situ microbial biomass (White, Pinkart, and Ringelberg 1996); community composition (White, Stair, and Ringelberg 1996; Ringelberg, Sutton, and White 1997), and degradation potential (Knaebel and Crawford 1995). Analysis of bacterial polar lipids provides information on microbial biomass and community composition and the

changes therein resulting from anthropogenic chemical perturbations (White et al. 1997). In addition to microbial biomass and community composition, analysis of nucleic acids identifies genes encoding enzymes required for explosive degradation and demonstrates the presence of these genes in situ.

Use of these molecular methods in conjunction with microcosm studies employing ^{14}C-labeled contaminants permits assessment of the potential for a site to attenuate the contaminants by microbial processes. The radioassay provides direct evidence that transformation and/or complete mineralization can occur in materials from the site under laboratory conditions. This technique provides a measurement of the rate and extent of biologically mediated transformation or complete mineralization.

The radioassay and biomarker investigations support the second and third lines of evidence required in the EPA directive (EPA 1997) by providing information from microcosm studies on contaminated media from the site. Biomarkers provide the link between ex situ microcosm studies and in situ conditions. Biomarkers demonstrate whether a viable biomass (a) is present, active, and capable of metabolizing RDX and TNT, (b) contains catabolic genes necessary for in situ degradation, and (c) is positive correlated to explosive concentrations, geochemistry, and mineralization properties.

Objectives

The goal of this portion of the study was to evaluate the ability of indigenous microorganisms to degrade explosives present in the contaminated aquifer at Site L1. Specific objectives included the following:

a. To provide evidence for the presence of a viable microbial biomass having the potential to mineralize explosives in microcosms.

b. To demonstrate the presence of in situ explosive mineralization potential based on genetic potentials.

c. To demonstrate the presence of suitable in situ microbial communities in terms of composition and physiological status.

d. To link laboratory and field evidence in a form that will demonstrate the presence or absence of natural attenuation processes based on biomarkers and provide estimates of the rates of explosive degradation/transformation.

Description of Study

Vertical profile sampling and sample processing

The protocol for handling and homogenizing soil samples was essentially that developed for the natural attenuation of explosives in soil and water systems at Department of Defense sites and applied at the Louisiana Army Ammunition Plant (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"; Pennington et al., "Protocol for Evaluating and Implementing Natural Attenuation at Explosives-Contaminated Sites").

a. Vertical profile samples were taken from three locations, S3, S4, and S5 (Figure 9). The cores were removed from the ground using a cone penetrometer with a stainless steel split-spoon sampler (45.7-cm (18-in.) inside length by 2.54-cm (1-in.) inside diameter). The sampler had been previously scrubbed and sterilized for 10 min in a solution containing 20-percent household bleach and 0.01-percent detergent, followed by rinsing with a steam sprayer. The sampler was checked for sterility by wipe-testing the inside and outside of the sampler with sterile 0.45-μm fiberglass Millipore filter (Millipore, Inc., New Bedford, MA). The filters were returned to WES by Federal Express on ice in a sterile Whirl Pak bag. Sterility of the filters was determined by placing the filters on nutrient agar plates, incubating for 48 hr at 30 °C, and checking the agar for growth.

b. Upon return of the split-spoon sampler to the surface, the core sample was removed by fully opening the sampler and sliding the contents into 1-L sterile Whirl Pak bags. The bag was sealed immediately, labeled as to exact location and depth, and placed on ice for shipment to WES.

c. Upon arrival at WES, the sample was removed from the bag and placed onto a sterile No. 4 sieve (screen mesh size 4.75 mm) fitted with a sterile catch pan. All operations were conducted in a GermFree fully vented biofume hood. Using a sterile spatula, the soil sample was smeared over the surface of the sieve screen continuously until all material small enough to pass the screen was forced through. The catch pan and sieve were separated, and the sieve was placed into a basin of soapy water outside the hood for decontamination and resterilization.

d. The sieved material was thoroughly mixed to ensure homogenization, and subsamples were allocated for each of the following tasks:

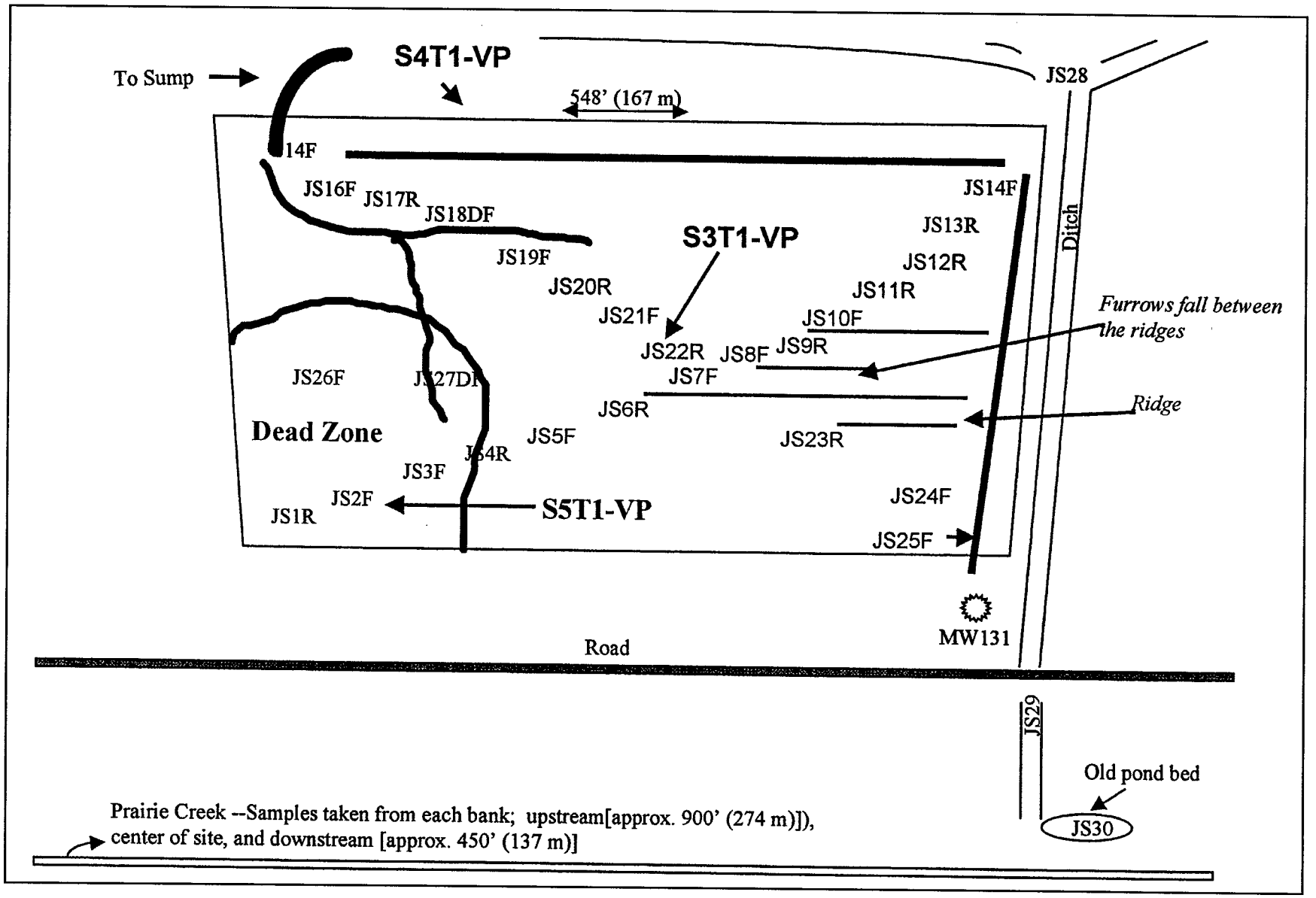

Figure 9. Location of vertical profile samples and surface samples from the ridge and furrow system

Task	Wet weight, g
DNA analyses	84
Microbial lipid analyses	84
Radiorespirometry	160
Explosives analyses	20
Phytoremediation	1
Particle size analysis	67
Other geochemical analyses	121
Total	537

All samples were stored in Whirl-Pak bags. All samples except those slated for radiorespirometry were immediately frozen at - 80 °C until used.

Surface soil sampling and processing in the ridge and furrow system

To further characterize the extent of explosives contamination at JAAP, a series of surface cores were taken in two perpendicular transects crossing the ridge and furrow system. Individual surface cores, designated "JS" followed by the sample number, were taken at approximately 40-ft intervals (Figure 9). The exact length of the sample intervals was varied to obtain materials from both ridges and furrows. Several additional samples were taken from Prairie Creek (Figure 9). Surface soil samples were collected as follows:

a. The sample coring devices were 5.08-cm (2-in.) diameter by 72.2-cm (28-in.) length sections of PVC pipe. Individual coring devices were soaked in bleach, washed with a steam cleaner, and checked for sterility, as was the stainless steel split-spoon used for collecting the vertical profile samples.

b. A threaded adapter was attached to the CPT truck to hold the PVC coring device in place. The CPT pushed the coring device into the soil to the depth of the device (72.2 cm (28 in.)) and then retrieved the device from the soil. The top and bottom of the sample were marked on the coring device, and the ends of the device were capped. The coring devices with samples were packed on ice and shipped to WES.

c. Upon arrival at WES, coring devices were scored along the length of two sides using a table saw. Coring devices were then capped with parafilm and held at 4 °C until processed. The soil cores were split apart under aseptic conditions, and the samples were removed and homogenized as described for vertical profile samples.

d. Soil transect samples were allocated as follows:

Task	Wet weight, g
Explosives analyses	10
Particle size	70
DNA and lipid biomarkers	60
Phytoremediation	1
Geochemistry	132
Other analyses	60
Total	333

Mineralization

These tests are conducted to quantify the presence of active microorganisms in a soil sample and determine their ability to mineralize explosives. Positive results provide evidence that microorganisms in the site have the capability to destroy the explosives. This constitutes evidence of microbial degradation as a mechanism of natural attenuation of explosives at the site. The test requires that 30 percent (w/v) slurries of soils freshly obtained from the field be challenged with ^{14}C-acetate, ^{14}C-TNT, ^{14}C-RDX, or other contaminants of interest. The slurry microcosms were evaluated for their ability to produce $^{14}CO_2$. The results provide (a) predictions of the rate and extent of explosives mineralization occurring at a specific location and (b) a relative indication of the viability of the biomass at the sites. Details of the procedure are provided in Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report" and "Protocol for Evaluating and Implementing Natural Attenuation at Explosives-Contaminated Sites."

Lipid biomarkers

This analysis provides quantitative data on the in situ viable microbial biomass, community composition, and physiological status. The viable microbial biomass in the environmental sample is estimated from the concentration of ester-linked phospholipid fatty acids (PLFA) from a single test tube extraction of the original sample. PLFA are analyzed via gas chromatography following recovery in a single phase solvent extraction and fractionation on a silica gel column. PLFA data are quantified by comparison with known internal and external standards and for patterns and types of PLFA profiles determined from a growing database (Federle et al. 1986). Results were related to results of the mineralization assays. This provided two independent determinations of the effects of the contaminants on the soil microbiota in situ. A detailed description of this analysis is provided in Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report" and "Protocol for Evaluating and Implementing Natural Attenuation at Explosives-Contaminated Sites."

Nucleic acid biomarkers

Rates of contaminant biodegradation in laboratory microcosms are related to the presence of bacterial degradative genes. Therefore, the ability to determine the presence of specific degradative genes will support natural attenuation or in situ bioremediation. Gene densities are related to rates of contaminant transformation defined in radioassays. The procedure requires isolation of DNA from soil, followed by amplification of bacterial biodegradation genes targeted to nitroaromatic contaminants. The presence of the targeted catabolic genes is correlated with radioassay results to establish the linkage between the presence of the requisite genes in the soil and the observed mineralization activity. A detailed description of this analysis is provided in Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report" and "Protocol for Evaluating and Implementing Natural Attenuation at Explosives-Contaminated Sites." Exceptions are as follows: total DNA was extracted from 0.5-g samples using a mini-beadbeater (Borneman et al. 1996) and analyzed by multiplex polymerase chain reaction. Triplicate subsamples were extracted from cores to account for sample heterogeneity.

Data handling and analysis

Correlations between ^{14}C-acetate, ^{14}C-RDX, and ^{14}C-TNT mineralization for each soil-isotope combination were run against values for total nucleic acids, total lipids, total explosives and TNT explosive transformation products, and various geochemical parameters. These were performed using the Pearson Product Moment Correlation or the Spearman Rank Order Correlation in the SigmaStat Statistical Software Package (Jandel Corporation, San Rafael, CA). Regression equations fit to the mineralization kinetics were obtained with the use of simple linear regression, polynomial regression, and nonlinear regression analyses in the same statistical package. Multivariate statistical analysis in the form of a principal components analysis and a hierarchial cluster analysis were performed on arcsin-transformed percentages of polar lipid fatty acid methyl ester concentrations and combinations of genetic markers using the Statistica Statistical Software Package (Statsoft 1995, Statsoft, Inc., Tulsa, OK).

Results and Discussion

Contaminants

TNT and RDX. Concentrations of TNT in the vertical profile and in the surface soil samples taken in the ridge and furrow system were moderate to low (Tables 10 and 11). TNT levels approached or exceeded 1,000 mg kg^{-1} in only three samples, JS-8, JS-10, and JS-19 (Table 11), while the concentrations at all of the remaining locations averaged 37.09 ± 17.24 mg kg^{-1} (± standard error). TNT was found in all of the Prairie Creek stream sites (Table 12), but was not

Table 10
Explosives Concentrations in Vertical Profile Samples (mg kg^{-1})[1]

Sample	Depth m	2,6DANT	TNB	TNT	2ADNT	4ADNT	2,6DNT
S3-T1-VP	0.23	0.158	BD[2]	0.580	0.504	0.269	0.130
	0.99	BD	BD	BD	BD	BD	BD
	1.95	BD	BD	BD	BD	BD	BD
	2.82	BD	BD	BD	BD	BD	BD
	4.33	BD	BD	BD	BD	BD	BD
	4.91	BD	BD	BD	BD	BD	BD
S4-T1-VP	0.23	BD	BD	BD	BD	BD	BD
	1.14	BD	BD	BD	BD	BD	BD
	1.78	BD	BD	BD	BD	BD	BD
	2.39	BD	BD	BD	BD	BD	BD
	3.14	BD	BD	BD	BD	BD	BD
	5.58	BD	BD	BD	BD	BD	BD
S5-T1-VP	0.23	BD	1.52	0.041	0.115	BD	BD
	0.87	BD	0.004	BD	BD	BD	BD
	1.54	BD	0.032	BD	BD	BD	BD
	2.66	BD	0.089	BD	BD	BD	BD
	3.38	BD	0.251	BD	0.043	BD	BD

[1] The compounds RDX, 2,4DNT, 2,4DANT, 1,4DNB, 1,3DNB, nitrobenzene, 2- nitrotoluene, 3-nitrotoluene,4-nitrotoluene were below the detection limit for each depth within each profile. Therefore, these analytes do not appear in the table.
[2] BD = Below detection limit.

found below the surface in the three vertical profile sites (Table 10). These results suggest that some mechanism had removed TNT. RDX was not found in any of the vertical profile samples (Table 10), but was found at low levels in five surface soil samples collected in the ridge and furrow system and in one stream sample (Table 12).

TNT transformation products. The transformation compounds 2,6DANT, 2,4DANT, 1,4-dinitrobenzene (1,4DNB), 1,3-dinitrobenzene (1,3DNB), 2ADNT, 4ADNT, 2,4DNT, and 2,6DNT occurred sporadically in the micrograms-per-kilogram (ppb) to low milligrams-per-kilogram (ppm) level over the surface in both the vertical profile samples (Table 10) and in the surface soils from the ridge and furrow system (Table 11). Only one low-level detection, 2,6-DANT at 0.59 mg kg^{-1}, was observed in the Prairie Creek samples (Table 12). Means ± the standard error of the mean were as follows:

Contaminant	Mean concentration ± standard error (mg kg^{-1})
2ADNT	4.495 ± 1.037
4ADNT	2.349 ± 0.829
2,4DNT	0.723 ± 0.188
1,3DNB	0.195 ± 0.099
1,4DNB	0.158 ± 0.081
2,6DNT	0.092 ± 0.049
2,6DANT	0.079 ± 0.031
2,4DANT	0.001 ± 0.001

The transformation products nitrobenzene (NB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT) were not detected in the vertical profile samples. The compounds 3- and 4-NT occurred rarely and in low concentrations in the surface soil samples from the ridge and furrow. Each of these compounds can be produced by microbial degradation of TNT, or by abiotic processes, e.g., photodegradation to the nitrobenzenes. The 2,4DNT and 2,6DNT and the nitrotoluenes are also by-products of TNT manufacture. Based on this information, TNT transformation or degradation is an active process at the site.

Photodegradation products. Trinitrobenzene (TNB), a photodegradation product of TNT, was prevalent over the entire site. While TNB may have been introduced with the initial contamination, ample opportunity for photodegradation existed in the ridge and furrow system to produce the quantities observed. TNB occurred in each of the vertical profile samples taken from Site S5-T1-VP, but did not occur in the vertical profile samples from Sites S3-T1-VP and S4-T1-VP (Table 10). TNB was present in most of the surface soils taken from the ridge and furrow system (Table 11). TNB was also found in one of the stream samples just above the detection limit (Table 12).

Summary. Low residual concentrations of TNT and RDX indicate that much of the original material has disappeared from the site. Detection of these explosives in the bed of the stream downslope from the site indicates that at least some of the contaminants have been flushed into the stream. Presence of both known biological intermediates and photodegradation products in surface soil samples and in some of the vertical profile samples indicates that the original contaminants have been degraded by physical, biological, and, possibly, abiotic chemical activities. Failure to find transformation products in the subsurface samples from the three vertical profiles indicates that the explosives have either not penetrated through subsurface materials or that attenuation mechanisms have removed the contaminants.

Table 11
Explosives Concentrations in Surface Soils Collected Across the Ridge and Furrow System (mg kg^{-1})

Sample	2,6ADNT	2,4ADNT	RDX	TNB	1,4DNB	1,3DNB	TNT	2ADNT	4ADNT	2,4DNT	2,6DNT	3-NT	4-NT
JS-1	BD[1]	BD	BD	5.01	BD	BD	1.98	1.61	0.32	BD	BD	BD	BD
JS-2	0.55	BD	BD	370.79	0.55	BD	13.66	3.58	BD	0.23	BD	BD	BD
JS-3	BD	BD	BD	4.61	BD	BD	5.58	0.71	0.14	BD	BD	BD	BD
JS-4	BD	BD	BD	BD	BD	BD	7.25	BD	BD	BD	BD	BD	BD
JS-5	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
JS-6	BD	BD	BD	1.03	BD	BD	2.97	2.14	2.65	BD	BD	BD	BD
JS-7	BD	BD	BD	1.94	BD	BD	100.94	10.31	BD	1.60	BD	BD	BD
JS-8	BD	BD	0.16	70.62	2.69	3.66	10,056.00	BD	BD	BD	BD	BD	BD
JS-9	BD	BD	BD	0.99	BD	BD	3.72	3.83	0.24	BD	BD	BD	BD
JS-10	BD	BD	0.09	35.36	0.35	0.38	1,676.57	19.31	16.17	1.83	BD	BD	0.12
JS-11	BD	BD	BD	1.05	BD	BD	2.87	3.77	0.59	0.57	BD	BD	BD
JS-12	BD	BD	BD	BD	BD	BD	0.74	1.29	0.10	BD	BD	BD	BD
JS-13	BD	BD	BD	1.15	BD	BD	2.37	1.72	BD	1.42	BD	BD	BD
JS-14	BD	BD	BD	0.69	BD	BD	3.18	1.01	BD	0.34	BD	BD	BD
JS-15	0.19	BD	0.01	1.06	BD	BD	2.48	0.46	BD	BD	BD	BD	BD
JS-16	BD	BD	BD	0.23	BD	BD	2.27	0.62	BD	BD	BD	BD	BD
JS-17	BD	BD	BD	0.47	BD	BD	4.71	1.96	0.56	BD	BD	BD	BD
JS-18	BD	BD	BD	0.36	BD	BD	4.76	1.04	0.10	BD	BD	BD	BD
JS-19	BD	BD	BD	7.48	BD	0.46	966.63	22.25	26.0	4.14	1.62	BD	0.92
JS-20	BD	BD	BD	1.60	BD	BD	16.61	11.16	3.57	1.66	BD	BD	BD
JS-21	BD	BD	BD	22.70	1.69	1.41	497.82	22.14	11.41	3.72	0.01	BD	BD
JS-22	BD	BD	BD	11.97	0.17	0.27	287.90	13.59	6.87	2.43	BD	BD	BD
JS-23	BD	BD	BD	2.22	BD	BD	3.83	9.37	2.24	2.79	BD	BD	BD
JS-24	0.13	BD	BD	0.16	BD	BD	0.61	0.23	BD	BD	BD	0.10	BD

(Continued)

[1] BD = Below detection limit.

Table 11 (Concluded)

Sample	2,6ADNT	2,4ADNT	RDX	TNB	1,4DNB	1,3DNB	TNT	2ADNT	4ADNT	2,4DNT	2,6DNT	3-NT	4-NT
JS-25	0.93	0.05	0.25	7.61	0.05	0.34	26.28	11.96	5.74	1.44	0.19	0.86	BD
JS-26	0.12	BD	BD	3.41	BD	BD	3.50	3.77	1.31	0.10	BD	0.32	BD
JS-27	0.22	BD	BD	2.62	0.60	0.06	3.29	0.93	0.40	0.33	BD	0.09	BD
JS-28	BD	BD	BD	BD	BD	BD	0.37	BD	BD	BD	BD	BD	BD
JS-29	0.11	BD	0.50	14.40	0.17	0.54	283.39	14.61	7.28	3.13	0.73	1.14	BD
JS-30	0.24	BD	BD	9.70	0.12	0.50	37.90	11.32	5.67	2.48	0.90	0.60	BD

Table 12
Explosives Concentrations in Prairie Creek Samples (mg kg^{-1})[1]

Sample and Location	2,6ADNT	RDX	TNB	TNT
BR549 UP: Upstream (Near Side)	BD[2]	BD	BD	2.55
BR549 UP-OPP: Upstream (Opposite Side)	BD	BD	BD	0.80
BR549: Midstream (Near Side)	BD	BD	BD	1.58
BRO: Midstream (Opposite Side)	BD	BD	BD	0.66
BRDO: Downstream (Near Side)	BD	BD	BD	1.89
BR549 D OPP: Downstream (Opposite Side)	0.59	0.35	0.01	6.06

[1] The contaminants 2ADNT, 4ADNT, 2,4DNT, 2,6DNT, 2,4DANT, 1,4DNB and 1,3DNB were below detection limits. Therefore, they were omitted from the table.
[2] BD = Below detection limit.

Soil geochemistry

Particle size and texture. Only vertical profile soils were assayed for particle size and textural properties. Soils were loamy to silty or sandy clay loam. Texture was independent of depth or vertical profile site location. Soils were typical of tall grass prairie sites (Buckman and Brady 1969).

Soil pH. Soil pH was measured on all of the soil samples from the vertical profiles (Table 13) and on nine of the surface soil samples from the ridge and furrow system (Table 14). With the exception of one acidic pH value at Site S4-T1-VP, all of the values for the vertical profile samples were nearly neutral to slightly alkaline (Table 13). The mean pH was 8.1 ± 0.2. The mean for surface soils from the ridge and furrow system was 7.9 ± 0.19. Alkaline pH levels are believed to encourage the formation of azoxynitrotoluenes (Funk et al. 1993), which may polymerize with each other and with complex soil organic matter. While azoxynitrotoluenes were not measured in these samples, these compounds are known biotic and abiotic transformation products associated with TNT-contaminated soils (McCormick, Feeherry, and Levinson 1976; Brannon, Price, and Hayes 1998).

Soil nutrients. Soil nutrients were determined for all of the soils in the vertical profile samples (Table 13) and nine of the surface soils from the ridge and furrow system (Table 14). Parameters were heterogeneously distributed in the soil profile with little apparent relationship between location and concentrations among the surface soils. The mean values for samples were as follows:

Parameter	Soil profile samples (mg kg^{-1} ± SE)	Soil profile surface and surface transect samples (mg kg^{-1} ± S.E.)
Total P	255 ± 20	237 ± 17
TOC	32,576 ± 3,082	24,442 ± 2,083
TKN	273 ± 34	364 ± 47
NO_2-N	2.88 ± 0.46	3.16 ± 0.93
NO_3-N	11.0 ± 1.0	8.94 ± 1.78
NH_3-N	7.5 ± 1.3	18.0 ± 3.5
SO_4	104.5 ± 20.9	49.9 ± 11.8

Relevance of soil characteristics. Soils were high in organic carbon, total phosphorus, and total Kjeldahl-nitrogen, had a loamy to sandy clay loam texture, and were generally mildly alkaline (Tables 13 and 14). The amounts found are expected to support vigorous activity by both bacteria and fungi. Population levels are expected to be well above those of mineral soils having organic matter levels of 1-3 percent at a neutral pH. Sufficient fine-grained material exists in the surface soils to provide for abundant microbial growth on the soil particles. The high levels for nitrogen and phosphorus in the vertical profile samples do not show any consistent trends with depth. The same is true for organic carbon; this is likely a consequence of the organic composition of these materials and the fact that organic carbon and the inorganic nutrient levels have been strongly influenced by decomposing plant material. The high organic carbon levels are probably able to support abundant activity by the soil microflora. This activity may include degradation of explosives or may support formation of a variety of TNT polymers under anaerobic-aerobic switching conditions (Rieger and Knackmuss 1995). These polymers are then able to complex with soil clay components (Rieger and Knackmuss 1995).

The pH and levels of nitrogen and phosphorus in the lower depths of the vertical profile samples are indicative of conditions supporting vigorous microbial activity as are the values for these components in the surface layers. A good distribution of surfaces (based on soil particle size) are available for microbial colonization throughout the soil profiles at all three sites except for the 14.2-ft sample at S3 and the 11.1-ft sample at S5. Generally, the abundance of available surfaces, the high levels of organic matter, and the moderate levels of total phosphorus, TKN, and inorganic nitrogen suggest that these environments are capable of sustaining moderate to high microbial populations. Considerable levels of microbial activity can be expected. The high levels of organic carbon also indicate that while these three sites may sustain vigorous aerobic activity at or near the surface, the environment may readily become anaerobic upon wetting due to high oxygen consumption levels by the microflora. This environment may provide a setting for the aerobic-anaerobic activities likely to degrade explosives and other complex contaminants. In addition, these rich granular prairie soils contain highly complex organic compounds derived from the abundant native and agricultural grass covers (Buckman and Brady 1969). Such

Table 13
Particle Size and Geochemical Composition of Vertical Profile Soil Samples

Sample	Depth ft	pH	Particle Size, %			Texture[1]	Geochemical Parameters, mg kg^{-1}						
			Sand	Silt	Clay		Total P	TOC[2]	TKN[3]	NO_2-N[4]	NO_3-N[5]	NH_4-N[6]	SO_4[7]
S3-T1-VP	0.75	7.8	57.5	27.5	15	Sandy Loam	148	18,900	291	4.30	16.4	18.5	3.2
	3.25	7.4	47.5	35	17.5	Loam	161	9,460	181	4.45	17.0	1.36	41.1
	6.40	8.4	57.5	22.5	20	Sandy Loam	266	32,600	225	4.40	9.58	6.80	42. 5
	9.25	8.4	55.0	22.5	22.5	Sandy Clay Loam	240	33,200	248	<1.05[8]	6.49	11.0	43.2
	14.2	8.7	80.0	15.0	5.0	Loamy Sand	151	51,300	54.9	<0.471	9.05	3.00	65.2
	16.1	8.4	57.5	32.5	10.0	Sandy Loam	182	42,300	160	1.40	8.19	<1.12	76.8
S4-T1-VP	0.75	7.1	50.0	40.0	10.0	Sandy Loam	266	34,600	639	4.02	17.6	16.3	32.3
	3.75	5.9	50.0	27.5	22.5	Sandy Clay Loam	169	5,740	103	5.68	7.98	3.56	39.5
	5.85	8.2	55.0	25.0	20.0	Sandy Clay Loam	267	27,400	240	4.34	6.40	3.63	101
	7.85	8.3	52.5	27.5	20.0	Sandy Clay Loam	299	30,800	332	4.24	8.55	7.97	61.1
	10.3	8.4	52.5	25.0	22.5	Sandy Loam	281	34,800	267	4.48	7.75	9.41	50.4
	18.3	8.4	52.5	25.0	22.5	Sandy Clay Loam	355	35,100	433	4.78	11.3	7.18	169
S5-T1-VP	0.75	8.6	47.5	27.5	25.0	Sandy Clay Loam	332	36,900	334	1.16	5.35	9.23	115
	2.85	8.5	45.0	27.5	27.5	Clay Loam	342	32,300	327	1.79	13.9	12.3	249

(Continued)

Table 13 (Concluded)

Sample	Depth ft	pH	Particle Size, %			Texture[1]	Geochemical Parameters, mg kg^{-1}						
			Sand	Silt	Clay		Total P	TOC[2]	TKN[3]	NO_2-N[4]	NO_3-N[5]	NH_4-N[6]	SO_4[7]
	5.05	8.3	47.5	27.5	25.0	Loam	347	34,300	317	1.46	7.85	7.69	281
	8.74	8.5	50.0	22.5	27.5	Sandy Loam	154	57,300	98.6	1.25	16.7	<1.12	155
	11.1	8.4	85.0	10.0	5.0	Loamy Sand	382	36,800	384	1.28	16.1	9.89	251

Table 14
Geochemical Composition of Selected Surface Soil Samples Collected in the Ridge and Furrow System

Sample	pH	Total P mg kg^{-1}	TOC[1] mg kg^{-1}	TKN[3] mg kg^{-1}	NO_2-N[4] mg kg^{-1}	NO_3-N[3] mg kg^{-1}	NH_4-N[5] mg kg^{-1}	SO_4[6] mg kg^{-1}
JS-4	8.3	209	26,700	141	1.35	<3.447	12.1	64.5
JS-5	7.8	319	23,500	370	1.99	<3.21	13.2	112
JS-6	7.8	257	18,300	214	2.48	11.2	6.50	110
JS-7	7.9	215	17,400	467	1.36	12.6	33.2	32.6
JS-8	7.9	142	19,300	314	12.5	17.0	22.1	31.7
JS-9	7.6	203	12,600	282	4.74	9.03	13.6	25.6
JS-10	7.9	276	22,800	687	1.54	5.35	49.3	27.8
JS-11	8.0	211	21.800	367	1.12	4.84	11.8	5.43
JS-12	8.0	268	30,500	256	1.33	7.95	10.6	38.8

[1] Total organic carbon.
[2] Total Kjeldahl nitrogen.
[3] Nitrate nitrogen.
[4] Nitrite nitrogen.
[5] Ammonia nitrogen.
[6] Sulfate.
[7] < Below detection limit

soils are likely to contain materials that require the microorganisms living on them to possess enzymes able to degrade complex compounds, which may include explosives.

Summary. Soils were very similar in the magnitude of the various geochemical parameters over the surface of the site and with depth in the soil profile sites. The soils were high in organic matter and capable of supporting extensive microbial activity. The alkaline pH may encourage the formation of explosives polymers under aerobic conditions. The high organic matter may enhance the development of anaerobic conditions in the soil following heavy rain events, contributing to the formation of reduction products that can polymerize under anaerobic-aerobic conditions. TNT and its transformation products will also tend to bind to organic matter in soil, and this may comprise an additional pathway for attenuation of TNT. The nutrient and organic carbon levels indicate that the site is able to support intense mineralizing activity and may provide cometabolites supporting degradation pathways for complex man-made organic compounds such as TNT and RDX.

Mineralization

The ability to mineralize substantial amounts of acetate within a short time frame (2-5 days) is an indicator of the overall good health of the soil microbial

communities at Site L1. Acetate mineralization was moderate to strong, indicating the presence of active microbial populations in the soil profiles (Table 15). Acetate mineralization at all depths of the soil profiles was generally distributed homogeneously (Figure 10, Table 15). Resident microbial communities exhibited the potential to mineralize RDX in the field at specific sites (Figure 11). Maximum rates usually occurred at middepth (Table 15). The average rate was 0.194 ± 0.020 percent[1] per day, or $0.174\ \mu g\ mL^{-1}\ day^{-1}$. The resident microbial communities exhibited the potential to mineralize TNT at a slow rate. The pattern for TNT mineralization activity with depth was quite different from that for RDX (Table 15, Figures 11 and 12). Substantial TNT mineralization (approximately 10 to 14 percent) occurred in the surface and near-surface samples at Site S4, while Site S3 had values in excess of 4 percent at comparable depths (Figure 12). Site S5 soils exhibited mineralization values at or near the TNT radiochemical impurity level of 3.0 percent. The average mineralization rate was 0.127 ± 0.031 percent[2] per day, or $0.334\ \mu g\ mL^{-1}\ day^{-1}$.

Total recoveries of the radioactivity originally added as acetate to soils averaged 82 percent (Figure 13). Total ^{14}C-labeled CO_2 was generally between 25 and 40 percent of the total amount added (Figure 13). Standard errors for the total mass balances were generally less than 10 percent of the mean. Most of the radioactivity originally added as RDX was recovered from the soil and aqueous phases, rather than as radiolabeled CO_2. This indicated a lack of RDX mineralization. Total recoveries from all phases averaged 89 percent of added radioactivity (Figure 13). RDX, while poorly soluble in water, has very little affinity for soils and a low affinity for nonliving organic matter. Thus, the radioactivity in the solid phase was likely a result of uptake by microorganisms that are known to accumulate and utilize RDX under both aerobic and anaerobic conditions (McCormick, Cornell, and Kaplan 1981; Binks, Nicklin, and Bruce 1995). Most of the radioactivity originally added as TNT was recovered from the soil and the aqueous phases, rather than as radiolabeled CO_2. Mass balances for ^{14}C recoveries ranged from 79 to 119 percent (Figure 13). Most of the radioactivity was associated with the solid phase. More radioactivity was associated with the solid phase than in the acetate or RDX tests.

Acetate mineralization studies demonstrated the presence of viable microorganisms in soil samples from all depths at the three profile sites. RDX mineralization exhibited a spotty distribution among the sites. TNT mineralization data showed pronounced activity in the surface and near surface layers except at Site S5 where no significant activity was observed. Mineralization of both RDX and TNT occurred very slowly. Nearly half of the acetate mineralized to CO_2, while most of the ^{14}C added as RDX or TNT remained in the aqueous and solid phases. This evidence suggests that RDX and TNT can be degraded microbially, and some mineralization occurs. However, mineralization was slow except in the surface and near-surface layers of some locations.

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[1] Test contained 5.21 μg per 30 ml.
[2] Test contained 10.02 μg per 30 ml.

Table 15
Mineralization Rates in Vertical Profile Samples (Values are the means of three replicates ± standard error)

Sample	Depth m	Acetate Rate %/Day	RDX Rate %/Day	TNT Rate %/Day
Site S3-T1-VP	0.23	6.52 ± 0.39	0.308 ± 0.011	0.235 ± 0.026
	0.99	5.34 ± 0.26	0.115 ± 0.007	0.145 ± 0.007
	1.95	7.16 ± 0.66	0.201 ± 0.127	0.073 ± 0.023
	2.82	4.70 ± 0.41	0.144 ± 0.008	0.046 ± 0.005
	4.33	7.04 ± 0.55	0.182 ± 0.005	0.035 ± 0.019
	14.9	8.22 ± 0.30	0.141 ± 0.026	0.028 ± 0.004
Site S4-T1-VP	0.23	8.42 ± 0.42	0.044 ± 0.009	0.500 ± 0.010
	1.14	4.96 ± 1.75	0.198 ± 0.074	0.354 ± 0.026
	1.78	7.30 ± 0.37	0.236 ± 0.018	0.116 ± 0.021
	2.39	6.40 ± 0.13	0.181 ± 0.023	0.062 ± 0.010
	3.14	5.54 ± 0.17	0.110 ± 0.006	0.028 ± 0.005
	5.58	3.24 ± 0.55	0.125 ± 0.008	0.025 ± 0.004
Site S5-T1-VP	0.23	4.62 ± 0.33	0.255 ± 0.027	0.138 ± 0.010
	0.87	6.46 ± 0.49	0.249 ± 0.005	0.093 ± 0.015
	1.54	6.54 ± 0.31	0.277 ± 0.020	0.128 ±0.021
	2.66	5.72 ± 0.43	0.161 ± 0.018	0.082 ±0.011
	3.38	6.24 ± 0.39	0.375 ± 0.012	0.069 ± 0.006

Lipid biomarkers

A substantial viable biomass was observed. Subsurface cell densities were approximately 10^6 cells g^{-1} dry weight of soil, two orders of magnitude less than those observed at the surface. Biomass decreased linearly with increase in depth at Sites S3 and S4, but remained relatively constant throughout the depth profile at Site S5 (Figure 14). Microbial community composition was primarily affected by geochemical fluctuations associated with an increase in depth. A plot of the distribution of gross bacterial functional groups emphasizes the transitions in community composition that occurred with increasing depth (Figure 15). Community compositional patterns also differed between sites, indicating some degree of heterogeneity across the site. For example, Site 3 showed a decrease in the gram-negative bacterial estimate, which can be related to fluctuations in contaminant exposure. Gram-negative bacteria have been identified as a significant variable. Site 3 was located adjacent to the ridge and furrow system,

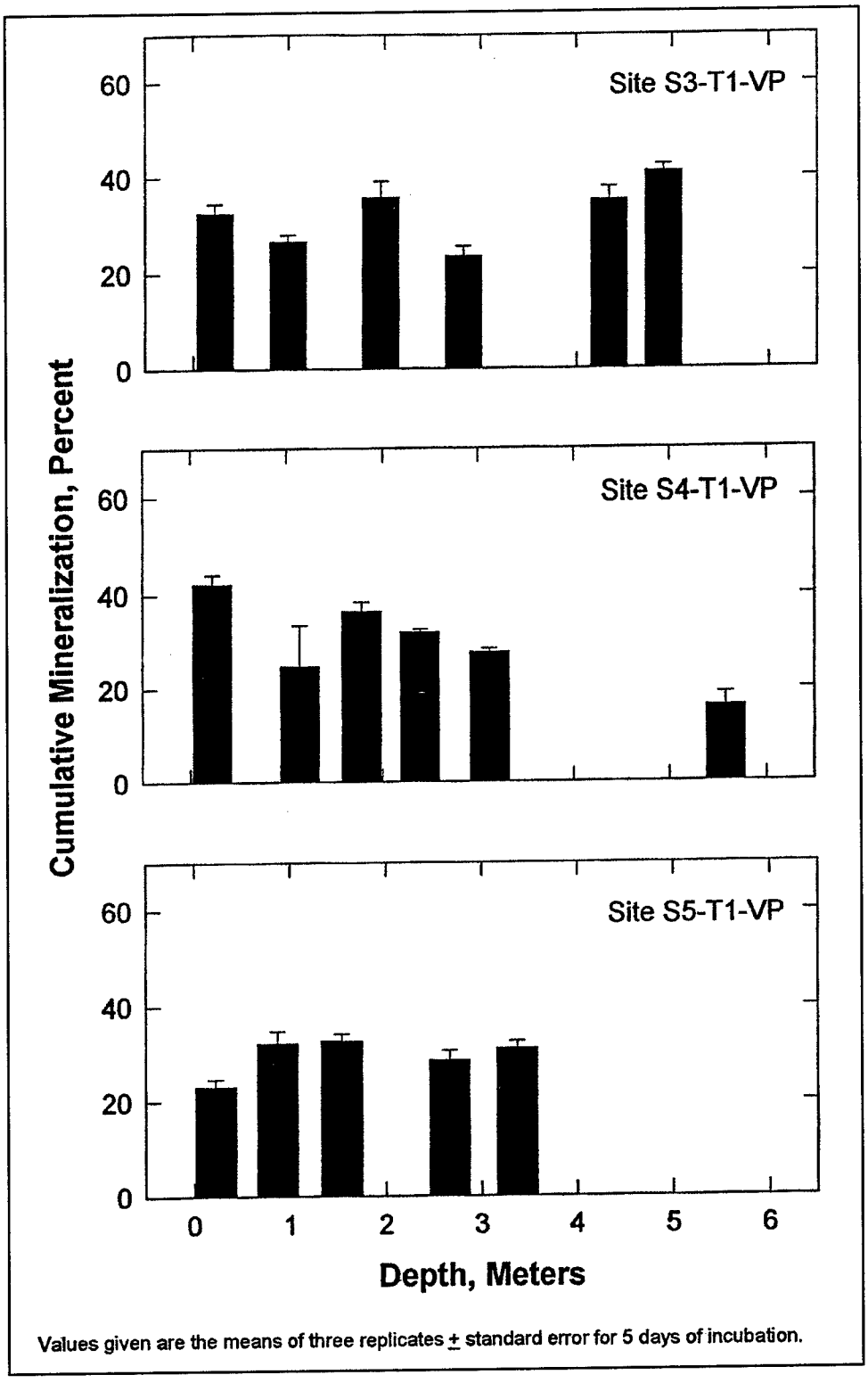
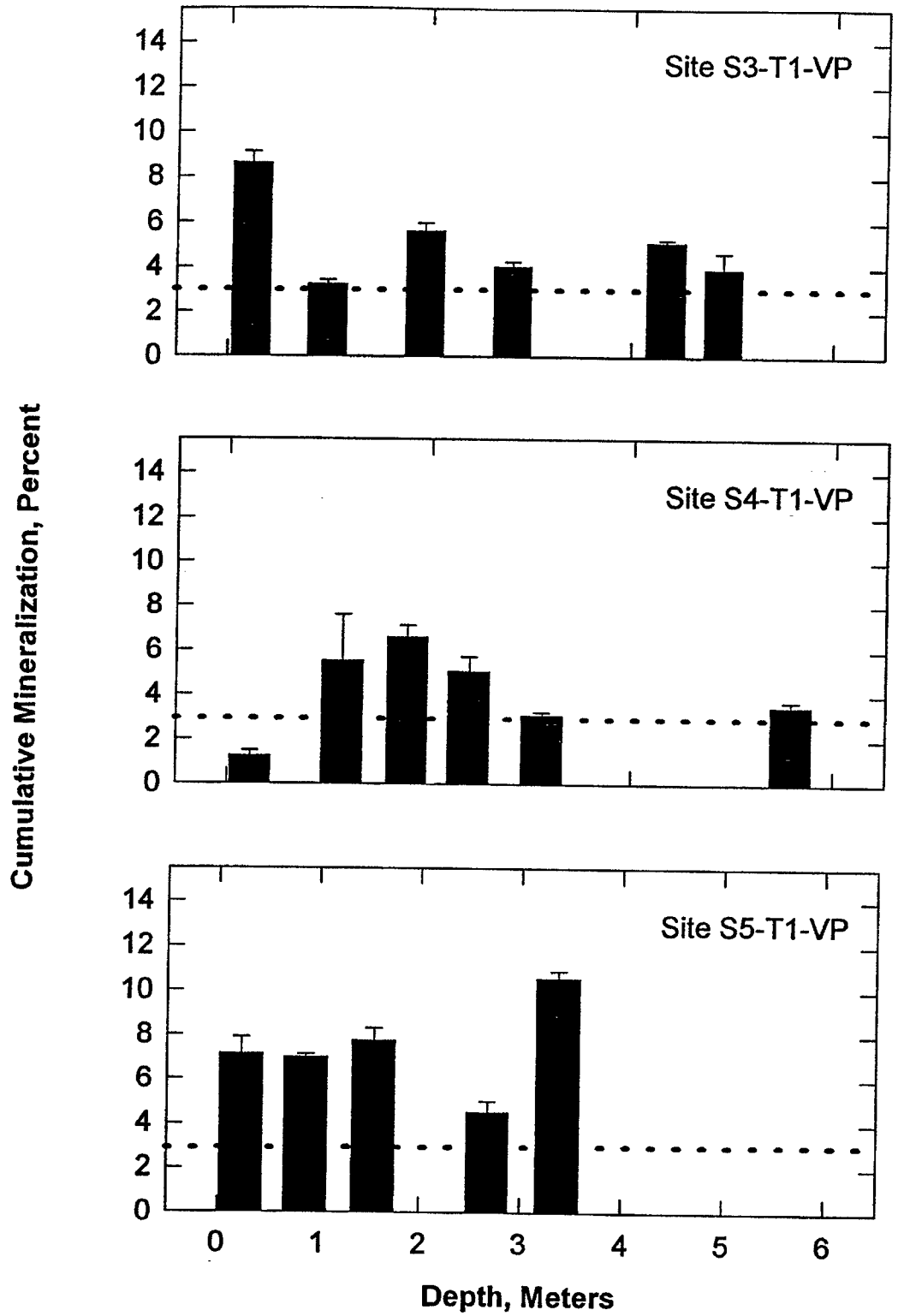


Figure 10. Acetate mineralization in vertical profile samples



Values given are the means of three replicates ± standard error for 28 days of incubation.
Dashed lines in each panel represent the level of impurities present in the radiolabeled RDX.

Figure 11. RDX mineralization in vertical profile samples

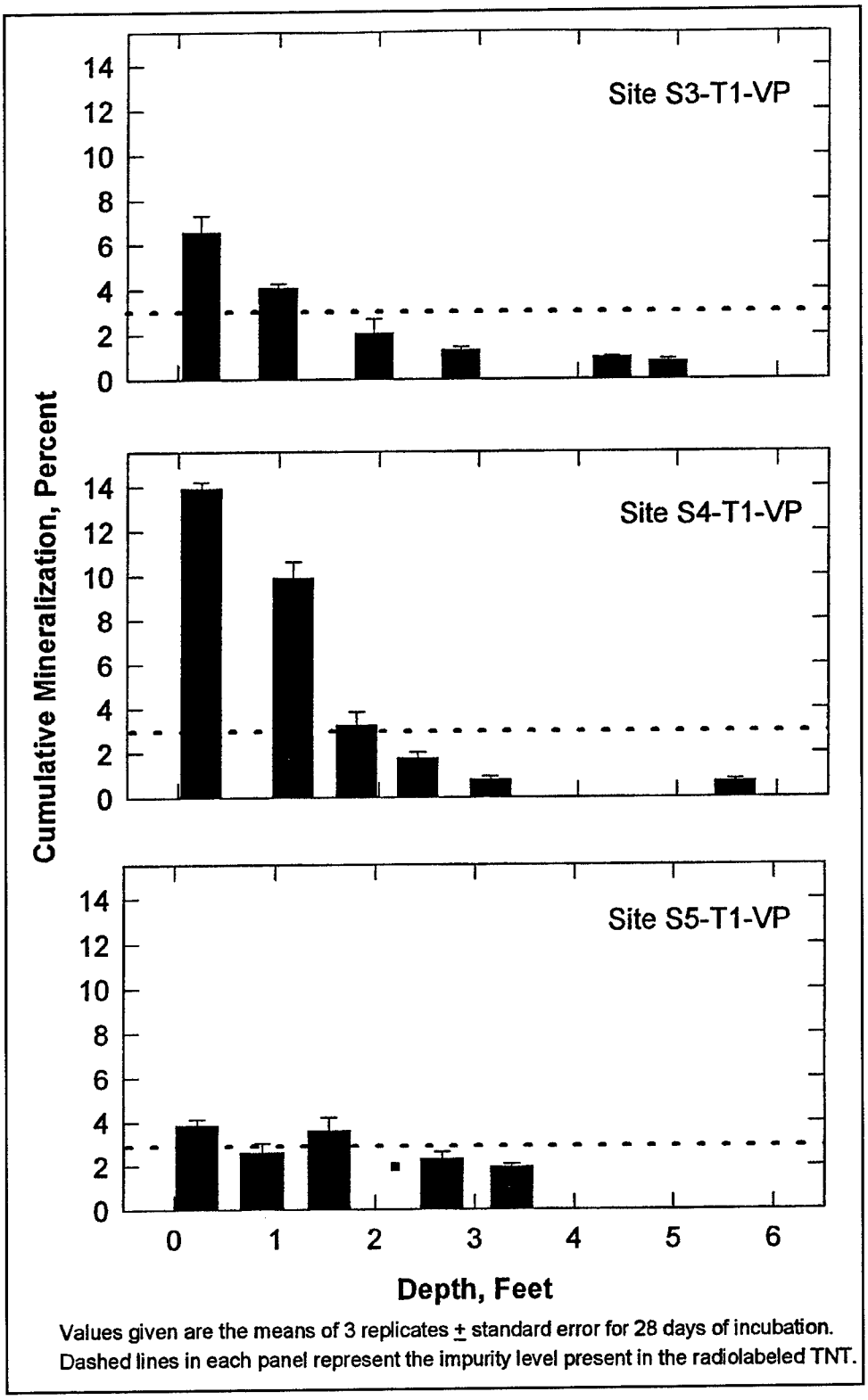


Figure 12. TNT mineralization in vertical profile samples

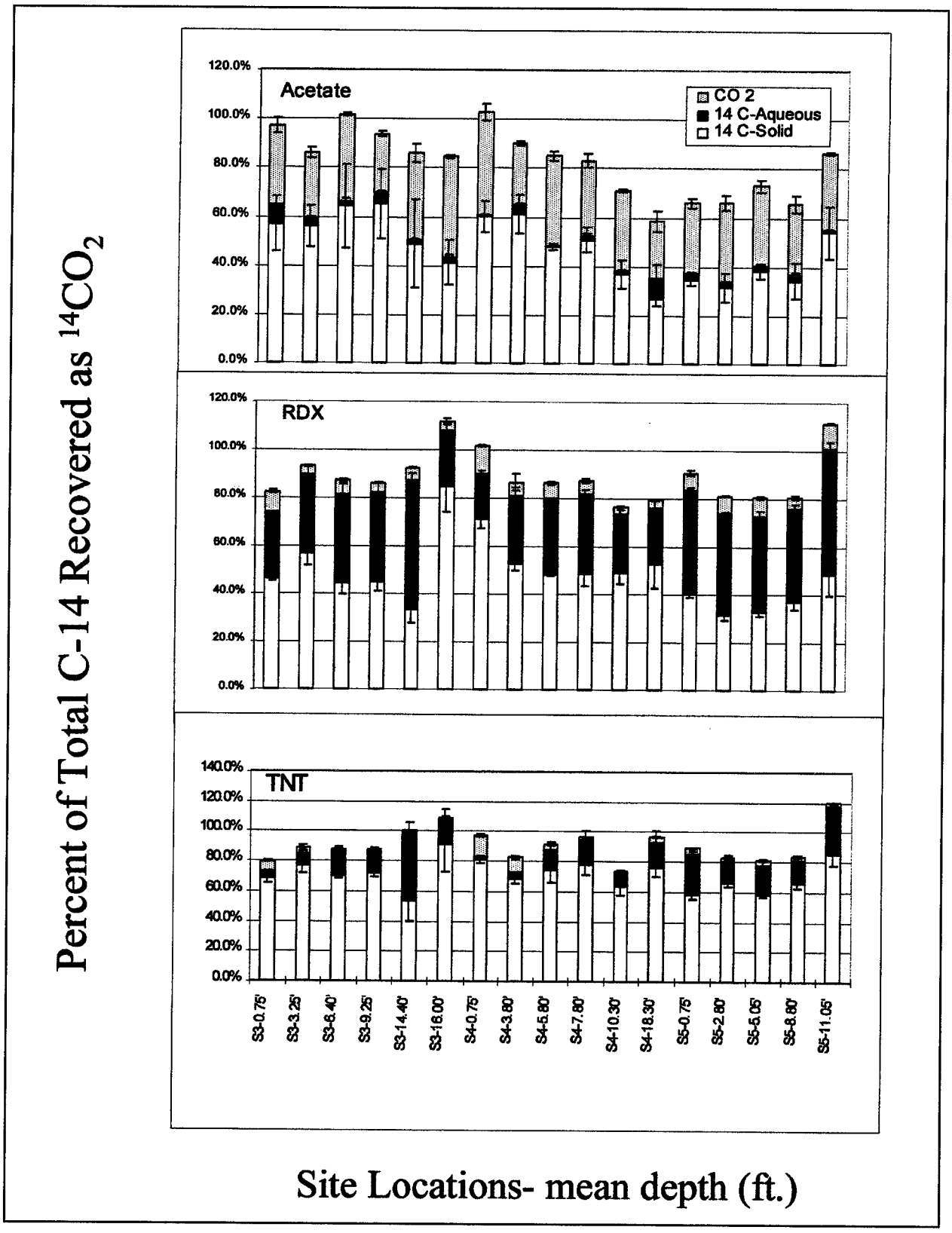


Figure 13. Mass balances for acetate, RDX, and TNT from vertical profile Sites S3, S4, and S5 at Site L1

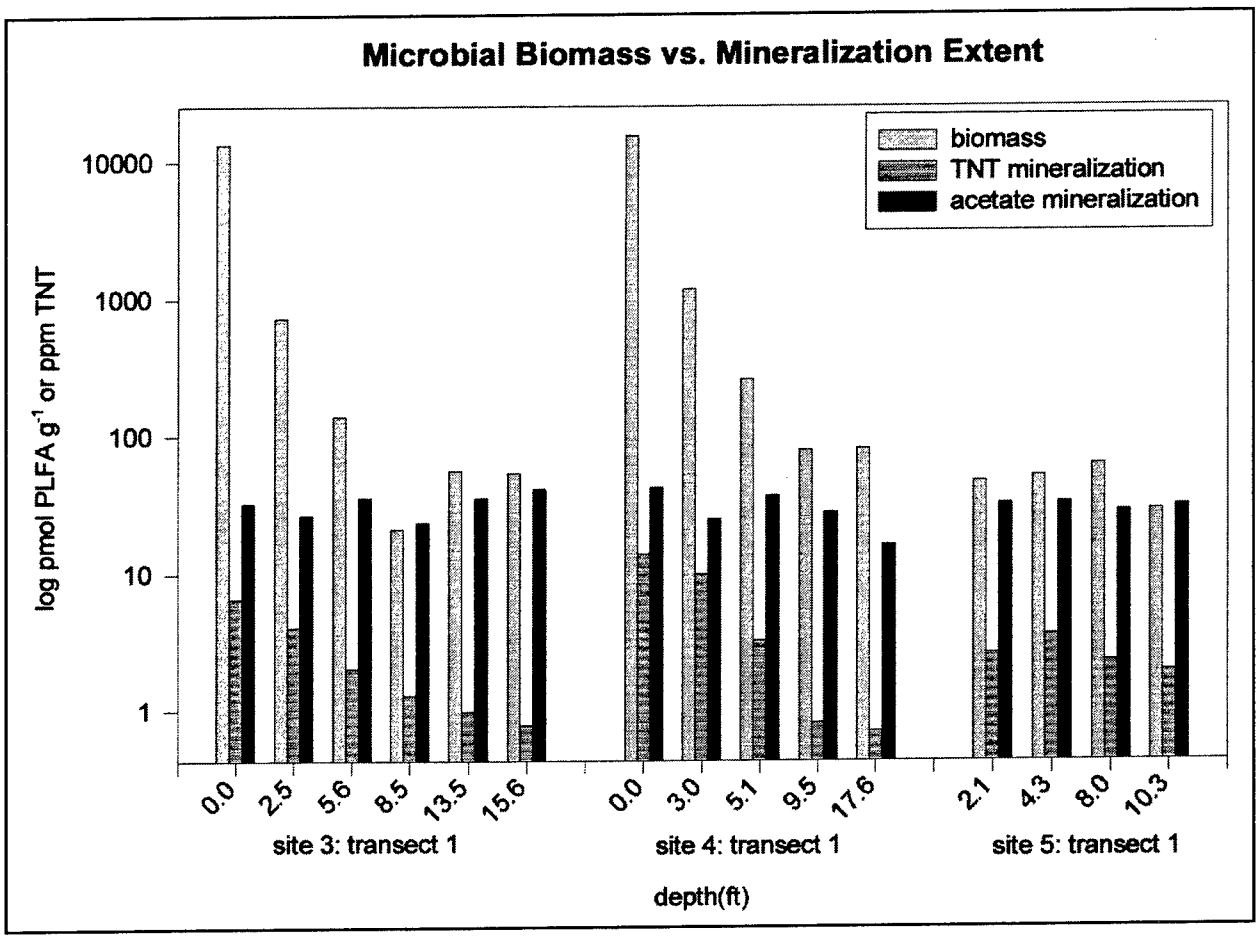


Figure 14. Microbial biomass based on PLFA results and extent of TNT and acetate mineralization

which showed very high surface soil TNT concentrations, while Site 5 was within the "dead zone" where concentrations of TNB were the highest.

Viable microbial populations were detected in the surface and subsurface. The detection of the lipid biomarkers in substantial amounts provided the in situ measure to which the ex situ respirometry measures could be compared and contrasted. The viable microbial biomass correlated significantly with rates of TNT mineralization. In addition, specific attributes of the microbial community were directly related to the mineralization of TNT. The relative percentages of lipid biomarkers representative of obligate anaerobes, more specifically the sulfate and iron-reducing bacteria, correlated positively with the TNT mineralization rates. A membrane lipid configuration often related to a microorganism's response to a toxicant also correlated positively with the mineralization of TNT. The significant relationships identified between the ex situ mineralization rates and the in situ community attributes suggest that indigenous microbial populations at the site are capable of biodegrading TNT and RDX.

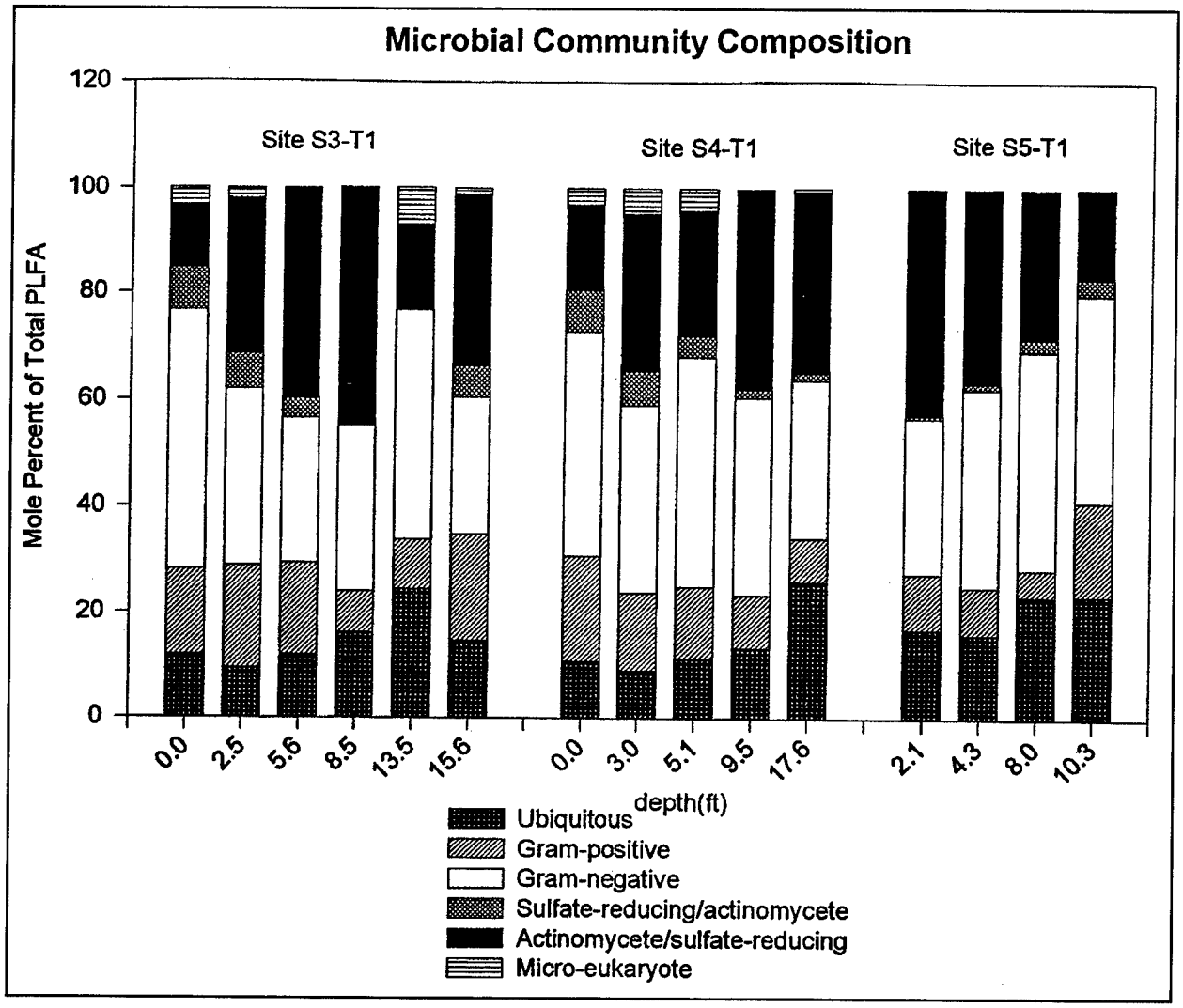


Figure 15. Microbial community composition in vertical profile soils

Nucleic acid biomarkers

Genes related to biphenyl extradiol dioxgenases (bph, NAD(P)H nitroreductases (nreduct), *Desulfovibrio* sp. dissimilatory sulfite reductases (dsrB), and catechol 2,3-dioxygenases (xylE-type c230) were found in each vertical profile sample (Figure 16). As was seen in analysis of soils from the Louisiana Army Ammunition Plant (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"), the number of different catabolic genes and presence or abundance of NAD(P)H nitroreductase, bph 250 bp, and biphenyl dioxygenases appear to be reliable biomarkers for contaminant presence and mineralization potential. Contaminant and daughter product concentrations are essentially measurements of onsite conditions. Therefore, correlation of genetic biomarkers to both contaminant

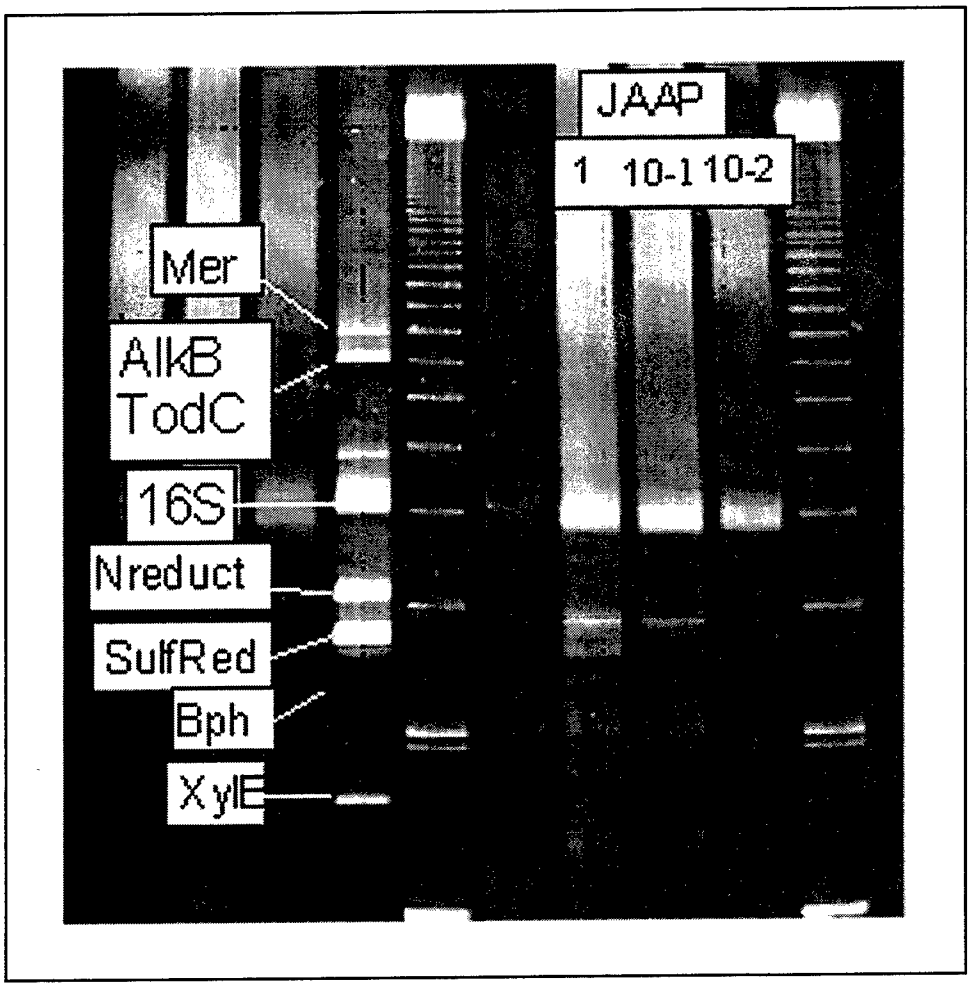


Figure 16. Detection of degradative genes

concentration and laboratory respirometry-derived mineralization data provides the bridge from flask data to actual field conditions.

Summary of biomarker results

Lipid biomarkers showed a linear decrease in biomass and communities with depth. The viable microbial biomass and specific microbial attributes were significantly related to TNT mineralization and to TNT mineralization rate. Specific nucleic acid biomarkers were found and were correlated with contaminant and transformation product concentrations and with mineralization data. Therefore, biomarker data provided a connection between laboratory microcosm and field results.

Correlation analyses

Significant correlations were found between the extent of acetate, RDX, and TNT mineralization and certain biomarkers, geochemical parameters, and contaminant concentrations (Table 16). Total acetate mineralization was positively correlated with a biphenyl hydrogenase gene probe (150 bp), negatively with a physiological stress attribute (cy19:0/18:1w7c), and negatively with the percent clay content. RDX mineralization was negatively correlated with a biphenyl hydrogenase gene probe (320 bp), but positively correlated with the presence of the contaminant 2ADNT reductase gene probes (125-380 bp). The latter probes were specifically used because of their suspected importance to the mineralization of TNT. TNT mineralization was also positively correlated to lipid biomarkers indicating total biomass, the relative percentage of certain anaerobes, specifically, sulfate-reducing and iron-reducing bacteria, to a measure of viable environmental stress, which is often induced by an exposure to a contaminant (18:1w7t/ 18:1w7c), and to an indirect measure of anaerobic respiration (i15:0/a15:0). TNT mineralization was also positively correlated with the percent silt content of the soil, but negatively correlated with TOC and pH.

The data do not indicate whether or not mineralization has played a substantial role in RDX disappearance over time. However, the general inability to find detectable levels suggests that RDX may have disappeared from soils quite some time ago. If so, little, if any, microbial activity against RDX may remain. The low levels of RDX mineralization observed in the radioassays as well as the undetectable levels of RDX contamination in the soils support this scenario.

In general, the results indicate the presence of several genes expected to be active in TNT mineralization and also suggest a role for anaerobic respiration, including iron and sulfate reduction. These results support the mineralization activity found in the radioassays. The negative correlation between TOC and TNT mineralization is unexpected, since soils having organic carbon appear to support higher levels of mineralization than do soils lacking this material (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"). However, the high organic matter content in Site L1 soils may provide a binding matrix strong enough to compete with microorganisms for TNT as a substrate. The negative relationship between pH and TNT mineralization is not surprising in view of the role of alkaline pH in enhancing azoxy polymer formation. The latter compounds are highly resistant to microbial degradation, tend to bind readily to sorptive surfaces (lowering their bioavailability), and are highly toxic to microorganisms (Funk et al. 1993).

Conclusions

Results of the biomarker investigations have important implications for two of the three lines of evidence. The second line of evidence requires

Table 16
Significant ($p < 0.05$) Positive Correlations of Biomarkers and Geochemistry with Mineralization Rates

Variable		Acetate Mineralization		RDX Mineralization		TNT Mineralization	
		Correlation	(p)	Correlation	(p)	Correlation	(p)
Nucleic Acid Biomarkers	NAD(P)H nitroreductase 380 bp					0.50	0.04
	dissimilatory sulfite reductase 320 bp			-0.54	0.02		
	biphenyl dioxygenase 250 bp					0.55	0.02
	atrazine reductase 150 bp	0.48	0.05			0.50	0.04
	unknown gene 125 bp					0.52	0.03
Lipid Biomarkers	Biomass					0.58	0.02
	Ubiquitous					-0.71	0.00
	SRB/IRB					0.60	0.02
	cy19:0/18:1w7c	-0.54	0.04				
	18:1w7t/18:1w7c					0.64	0.01
	i15:0/a15:0					0.74	0.00
Geochemistry	% Clay	-0.49	0.05				
	% Silt					0.52	0.03
	TOC					-0.52	0.03
	pH					-0.56	0.02
Contaminant	2ADNT			0.62	0.01		

identification of mechanisms responsible for natural attenuation and determination of the rate. Results demonstrate that (a) TNT transformation products onsite include substances produced by abiotic processes and microbial activity, and microbial activity was present at Site L1; (b) site soils provide conditions supporting active microbial communities; (c) native microbial communities at Site L1 contain microorganisms known to participate in transformation/mineralization of explosives; (d) microbial communities in contaminated areas onsite possess genes suspected to be active in explosives degradation; and (e) the average rates of mineralization were 0.334 and 0.174 μg mL^{-1} day^{-1} for TNT and RDX, respectively.

The third line of evidence requires direct evidence showing the effectiveness of natural attenuation of explosives. Results from the vertical profile samples demonstrated that (a) viable, healthy microbial populations were present;

(b) potential for moderate RDX-mineralizing activity was present, but actual activity was low, perhaps reflecting the overall absence of RDX onsite; and (c) moderate-to-vigorous TNT-mineralizing activity occurred in the surface to near-surface layers of two of the sites, while no substantial activity was present in the third site, where TNB, a toxic photodegradation product, was present.

5 Numerical Modeling

Introduction

Numerical modeling is the most cost-effective means for the quantitative evaluation of multiple natural processes represented as a set of mathematical expressions, consistent with site-specific conceptualizations. The complex and incompletely understood processes involved in the natural attenuation of explosives require the computational power and flexibility of a numerical simulator. Defense of natural attenuation as a feasible remediation alternative under the scrutiny of regulatory entities necessitates the rigor afforded by numerical modeling.

The main objective of the modeling is to compliment the field monitoring and data collection for better demonstration and graphic representation of natural attenuation of explosives at Site L1 (Group 61) located at the load-assemble-package area (LAP). The modeling effort focuses on conceptualization of the site hydrogeology and reduction of explosives by processes such as immobilization/ degradation and first-order decay.

The Department of Defense Groundwater Modeling System (GMS) (1966) with its subsurface model, FEMWATER (Lin et al. 1997), was selected for the modeling element of this study. GMS is a comprehensive computer graphical system. The GMS includes numerical tools to facilitate site characterization, site conceptualization, mesh and grid generation, geostatistical computations, and visualizations.

Site L1 is located in the north-central portion of the LAP area, north of Prairie Creek and southwest of the intersection of Chicago Road and Road 1 North (Figure 17). The study area covers approximately 80 acres and has been contami-nated by the use of a10-acre ridge and furrow system that received wastewater from washout operation (Dames and Moore, Inc. 1993). The topography in this area slopes southward toward Prairie Creek. Ground surface elevation ranges from 198 m (650 ft) above mean sea level (MSL) along the northern border of the site to 186 m (610 ft) above MSL along Prairie Creek. The area immediately north of Prairie Creek is wooded and generally dry. Prairie Creek is 10 to 15 ft wide and flows to the west from the eastern boundary

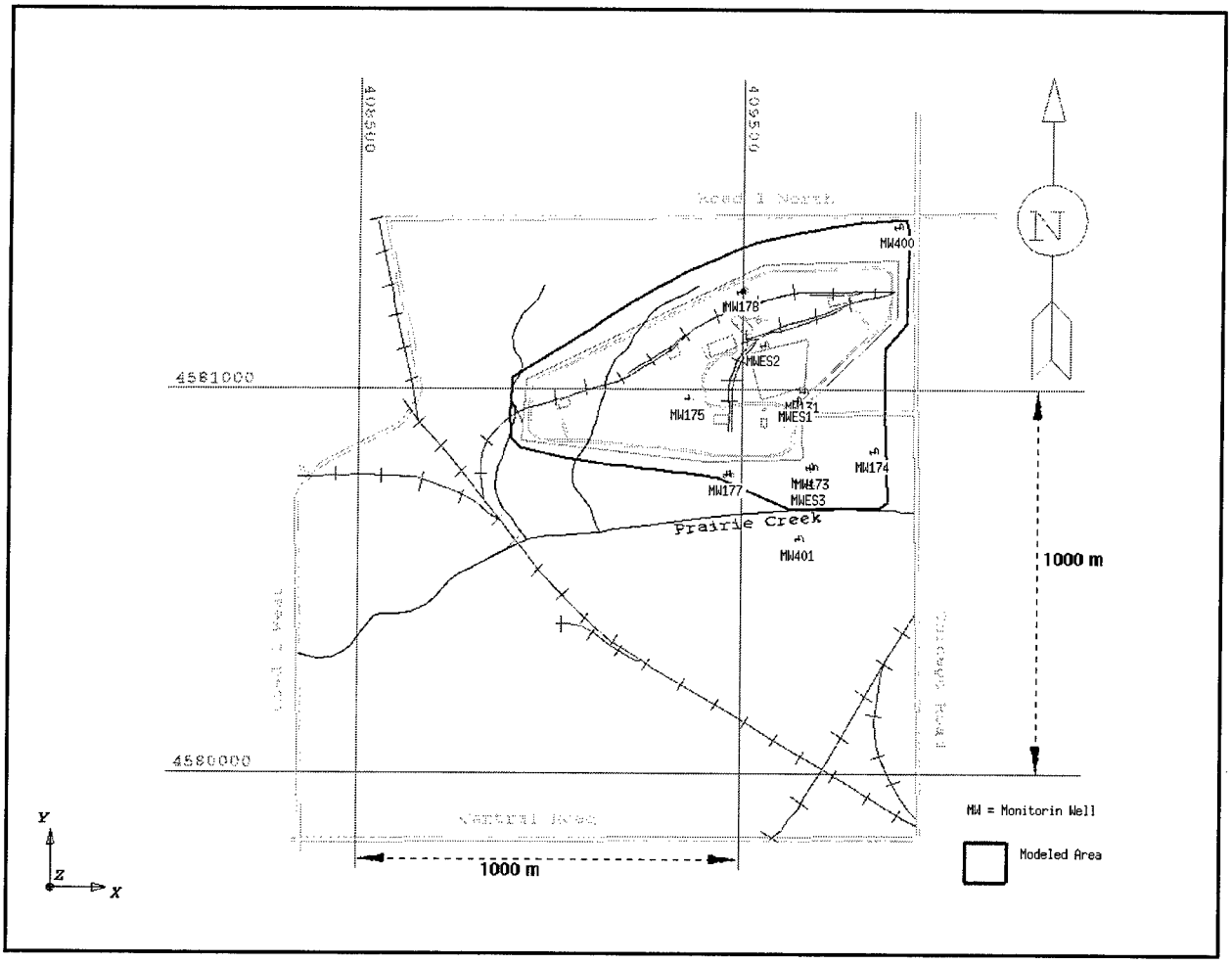


Figure 17. Schematic map of Site L1, Group 61 and surroundings (JAAP)

of the installation. Surface runoff from Site L1 flows into three drainage ditches that ultimately drain into Prairie Creek south of the site. Precipitation also ponds in low-lying areas east of the sump.

Subsurface conditions have been interpreted from the information provided in Dames and Moore, Inc. (1993), and cone penetrometer data collected by WES during 1997-1998. The descriptions given in the Dames and Moore report are based on review of lithologic logs of wells installed during the Phase 1 Remedial Investigation (Dames and Moore, Inc. 1993) and previous hydrogeologic investigations. Table 17 shows information on flow data collected at the monitoring wells during 1997-1998.

Table 17
Characteristics of Wells and Water Level Elevations for Each Sampling Round at Site L1

Well No.	Ground Elevation (above MSL)		Depth of well, m	Water Elevation, m									
	ft	m		05/17/97	06/12/97	07/11/97	08/09/97	09/06/97	10/02/97	10/31/97	12/02/97	01/12/98	03/18/98
MW131	623.05	189.91	6.50	186.248	185.943	185.599	185.227	185.020	184.877	184.694	184.874	185.736	187.330
MW172	613.58	187.02	10.58	185.145	185.032	184.709	184.508	184.520	184.486	184.550	184.599	185.090	186.320
MW173	613.41	186.97	3.60	185.291	185.139	184.8094	184.590	184.830	184.670	184.651	184.816	185.303	186.328
MW174	611.50	186.39	4.70	185.346	185.242	184.971	184.828	184.740	184.752	184.733	184.858	185.386	NS[1]
MW175	631.73	192.55	6.03	188.601	187.988	187.248	187.248	193.620	193.618	193.618	193.618	193.618	NS
MW177	614.63	186.39	9.46	185.510	185.410	185.069	184.810	184.834	184.681	184.748	184.812	185.492	186.864
MW178	640.75	195.30	14.24	188.686	188.263	187.498	185.943	185.426	185.242	185.166	185.120	187.132	NS
MW400	654.34	199.44	8.05	198.102	197.852	197.553	196.898	196.654	200.449	200.449	200.449	197.468	NS
MW401	617.84	188.32	12.53	186.306	186.672	186.459	186.391	186.641	186.669	186.620	186.855	186.937	NS
WES1	621.72	189.50	12.30	n[2]	n	n	184.944	184.803	184.684	184.684	184.700	185.562	188.11
WES2	636.31	193.95	11.69	n	n	n	185.520	185.200	184.962	184.895	184.861	186.385	188.747
WES3	603.97	184.09	11.78	n	n	n	182.400	181.813	182.368	182.460	182.499	182.987	184.166

[1] Not sampled.
[2] Not installed.

Conceptual Model

A conceptual model based on the site hydrogeological and chemical data was required before applying a numerical model to the site. The conceptual model is a powerful approach for abstracting and simplifying natural phenomena. The simplification is carried to the point where the model is still amenable to mathematical treatment, yet retaining critical hydrogeological conditions. To develop a complete conceptual model for Site L1, existing and new LAP hydrogeological data including borehole geologic data, hydraulic conductivity data, and flow boundary conditions were used.

The stratigraphy at Site L1 is divided into four units (Dames and Moore, Inc. 1993). The uppermost unit is composed of organic rich clays and silts with thickness ranging from centimeters at the northern portion of the site to a few meters near Prairie Creek. Yellowish-brown clays and silts ranging in thickness from 2 to 5 m (6 to 18 ft) underlie these. This unit overlies a discontinuous layer of clayey sand. This layer was encountered only in the boring for MW131. The basal unit consists of a discontinuous stratum that varies from clayey gravel to gravel, which may indicate mechanical weathering of the bedrock.

The cone penetrometer (CPT, stratigraphy) data were used to create four separate units described above using GMS (Figure 18). The original CPT data (Figures 18 and 19) did not include geologic layers where the monitoring wells were screened. Therefore, the fourth, lower layer was extended to cover the monitoring wells' screened zones (Figure 20).

Dames and Moore, Inc. (1993), reported a hydraulic conductivity of 9.2×10^{-6} cm sec^{-1} for the overburden, based on a slug test conducted on MW131 (Donohue and Associates, Inc. 1982a). This value is considerably lower than the average value of 1.7×10^{-3}cm sec^{-1}, based on slug tests performed throughout JAAP; silts and clays are the predominant soils beneath the site. A low value is typical for such deposits. The average hydraulic conductivity of the bedrock layer is reported to be 4.9×10^{-4} cm sec^{-1} based on slug tests from wells screened within the bedrock throughout JAAP. This is typical for dolomite (Freeze and Cherry 1979). The hydraulic conductivity for each layer of the modeling domain (Figure 21) was assigned based on the above hydraulic conductivity information (Table 18).

The source of flow recharge at Site L1 was assumed to be from rainfall. Average annual precipitation is 32-35 in. About 10-12 percent of the annual precipitation is estimated to reach the groundwater reservoir in Illinois (Suter et al. 1959).

The discrete data collected at the site were interpolated/extrapolated to estimate properties at intermediate points of the numerical grid. The GMS supports several geostatistical (interpolation/extrapolation) numerical tools. In the three-dimensional space, these included inverse distance weighting, natural neighbor, and kriging. Each of these approaches has merits. A combination of these tools was used to develop an acceptable conceptual model.

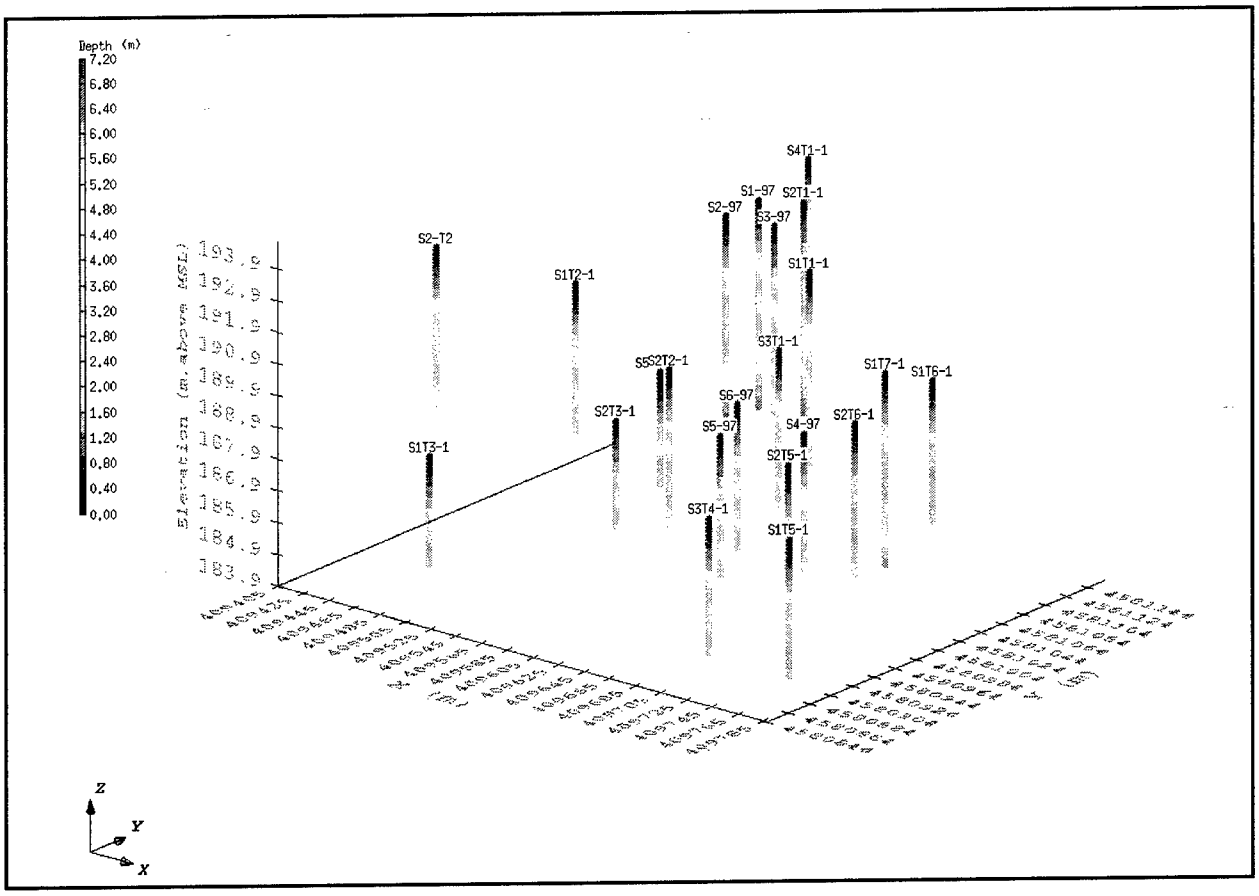


Figure 18. Original depth distribution of stratigraphy data, collected in 1997-98 at each CPT location

The only physical flow boundary of the site is located at the Prairie Creek. However, the numerical model required flow information at the other boundaries of the modeling domain. The water level elevations measured at the monitoring wells (Table 17) were used to estimate transient numerical flow boundary conditions.

Code Description

FEMWATER (Lin et al. 1997) is a three-dimensional finite element numerical code, which may be used to model flow and mass transport through saturated-unsaturated media. FEMWATER is an enhanced version of two models, 3DFEMWATER (flow) and 3DLEWASTE (transport). FEMWATER is integrated into GMS. GMS is a state-of-the-art graphical computer interface program. The flow equations in FEMWATER are based on the continuity and Darcy flow equations. The model application is limited by the assumptions

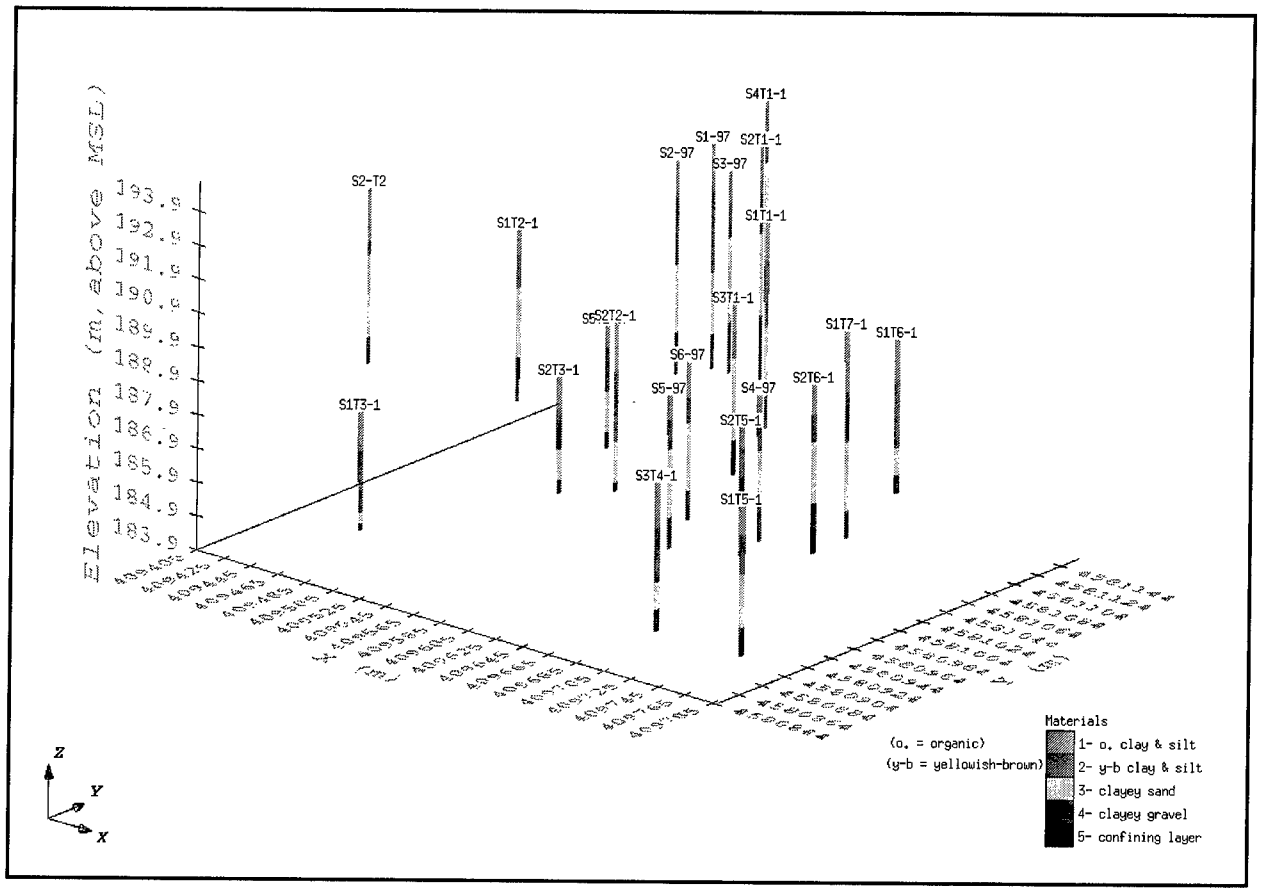


Figure 19. Stratigraphy averaged into four layers at each CPT location

applied to these equations. FEMWATER also can be used for density-dependent problems.

FEMWATER simulates the primary processes affecting dissolved-phase contaminant distributions in groundwater including advection, dispersion, sorption, and decay caused by chemical reactions and/or biological transformation. In most groundwater mass transport models, the biodegradation process has been assumed to follow zero- or first-order decay processes (Kosson, Agnihotri, and Ahlet 1995). FEMWATER uses the first-order decay as lumped biochemical decay.

FEMWATER requires three data sets containing soil parameters for unsaturated-saturated materials. In unsaturated flow domains, the hydraulic conductivity (K) varies with the soil potential head, h, which is also a function of the volumetric soil moisture content, θ. (A list of symbols and definitions is provided in Appendix A.) The required data sets provide the relationship between soil moisture content, relative hydraulic conductivity, and water content with the pressure heads. GMS has two options: the user can select an automatic generation of these parameters based on van Genuthen (1980) or input these

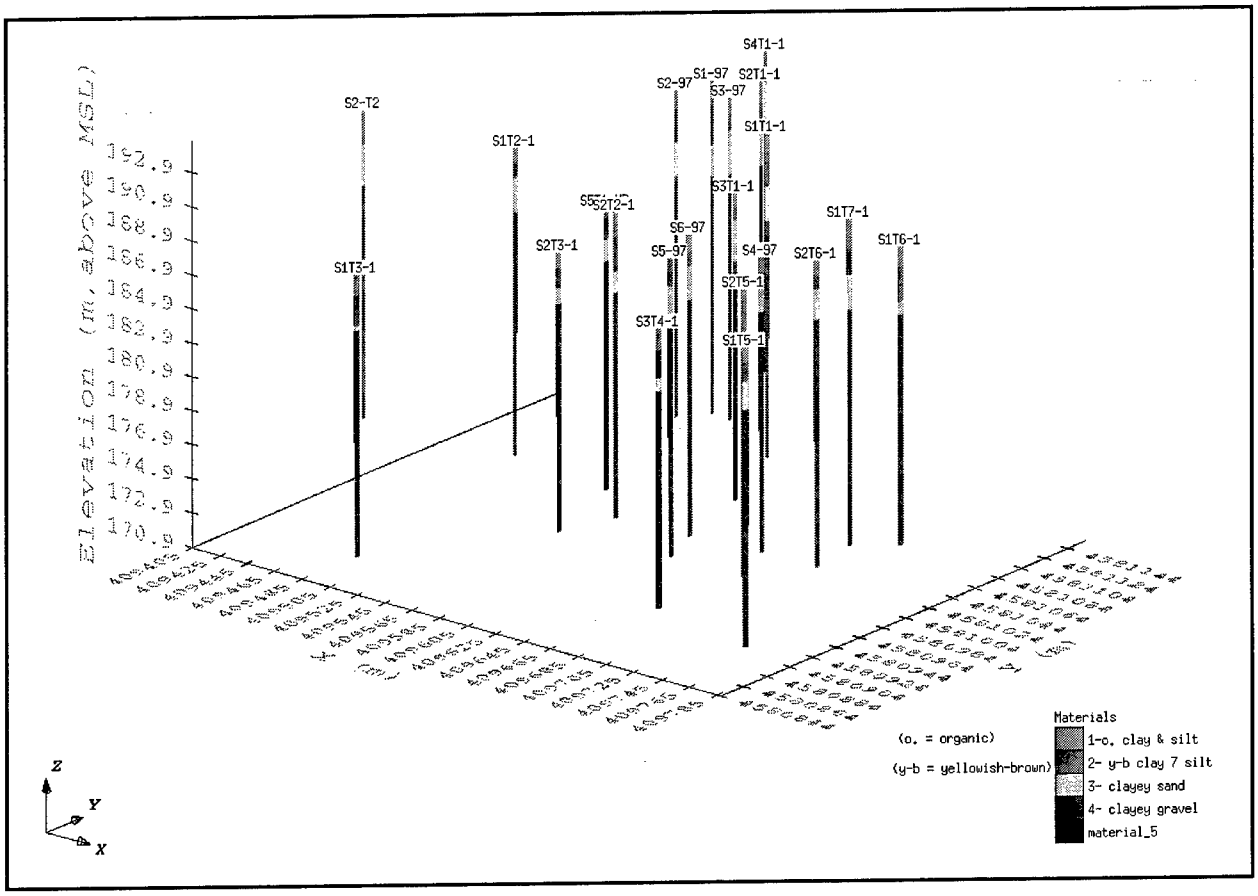


Figure 20. Stratigraphy averaged into four layers at each CPT location with extended bedrock layer

parameters manually. For the Site L1 application described here, Brooks and Corey 1964 formulations were used.

The Brooks-Corey formulations for moisture content, relative hydraulic conductivity, and water content are defined below.

The moisture content (θ) is defined as:

$$\theta = \theta_r (\phi\theta_r) \cdot \left(\frac{h_b}{h} \right)^{\lambda} \quad (1)$$

where

(θ_r) = residual moisture content (dimensionless)

ϕ = porosity (dimensionless)

h_b = bubbling or air-entry pressure (L)

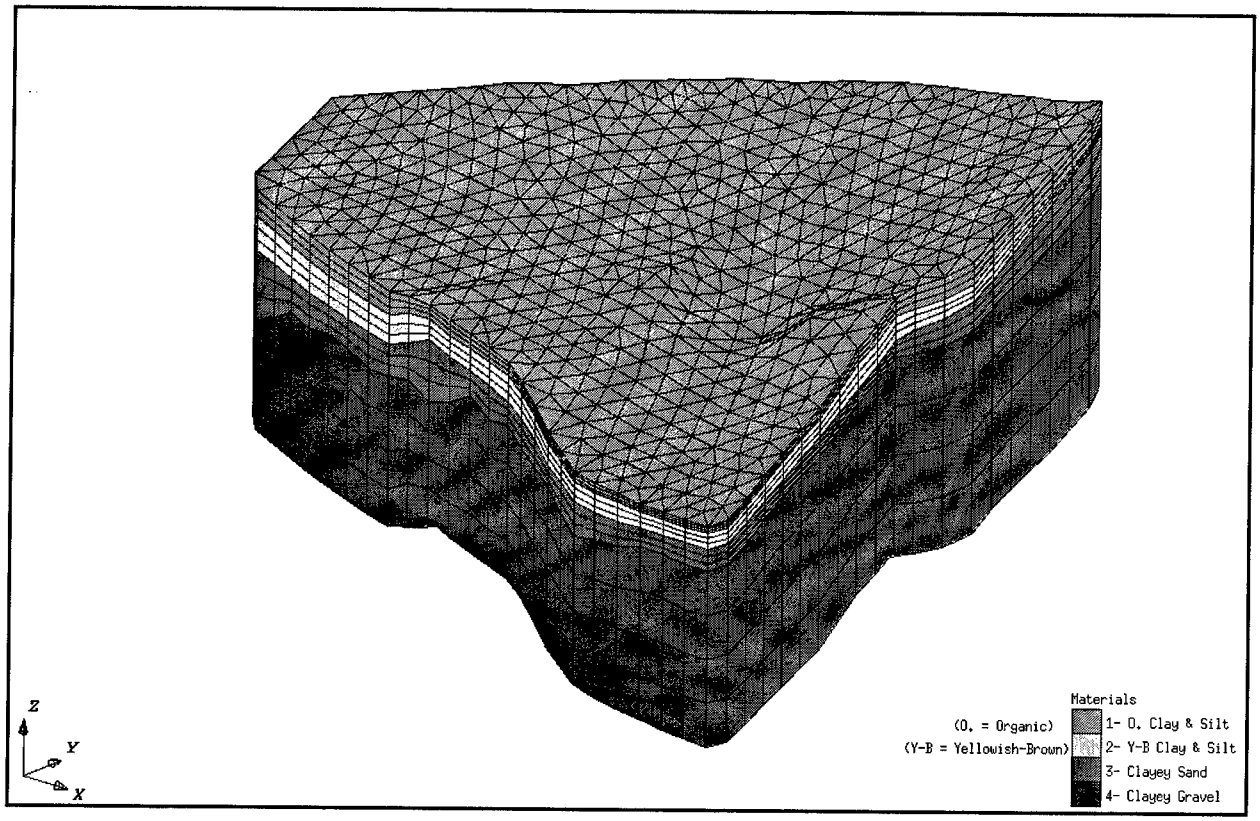


Figure 21. Three-dimensional mesh system used in FEMWATER for Site L1

Table 18
Hydraulic Conductivity of the Modeling Layers

Layer No. from above (Figure 21)	cm sec^{-1}	ft day^{-1}	m day^{-1}	Material
Layer 1	9.2E-06	0.026	0.008	Organic clay and silt
Layer 2	1.70E-03	4.82	1.469	Yellowish-brown clay and silt
Layer 3	1.7E-03	4.82	1.469	Clayey sand
Layer 4	4.90E-04	1.39	0.4234	Clayey gravel

h = pressure head (L)[1]

γ = pore size distribution index, which is a function of soil texture (dimensionless)

The relative hydraulic conductivity (K_r, dimensionless) is defined as:

[1] The upper case letters, L, T, and M, are used to denote generic length, time, and mass units.

$$K_r \left(\frac{h_b}{h}\right)^{(2\ 3\ \lambda)} \tag{2}$$

and the water content ($C_m(h)$, L^{-1}) is defined as:

$$C_m(h) = (\phi\theta_r)\left(\frac{\lambda}{h_b}\right)\left(\frac{h}{h_b}\right)^{(\lambda\ 1)} \quad \text{for } h \le h_b$$
$$C_m(h) = 0 \quad \text{for } h > h_b \tag{3}$$

The parameters used in Equations 1-3 must be determined for each soil type observed at the site. However, the determinations are costly and time-consuming. Therefore, published values for soil types, that match site soil characteristics are normally used in practice. Saturated hydraulic conductivity data (Site Subsurface Soil, Table 18) were grouped into three different classes of materials to match the Brooks and Corey parameters given in Table 19. These parameters were used in the above equations to calculate required unsaturated soil input data.

Table 19
Brooks and Corey Parameters Used in the Model

Soil Type	Saturated Hydraulic Conductivity *K*, m/day	ϕ	θ_r	$-h_b$	λ	Site Hydraulic Conductivity, m/day
Fine sand	2.1	0.377	0.063	0.820	3.7	1.47
Columbia sandy loam	0.7	0.496	0.110	0.850	1.6	0.42
Limon silt	0.013	0.449	0.000	0.338	0.22	0.008

Transport Equations

The governing equations for the transport part of FEMWATER are based on continuity of mass and advection/diffusion laws:

$$\theta_w\frac{\partial C}{\partial t}\ \rho_b\frac{\partial S}{\partial t}\ V\cdot\nabla C = \nabla\cdot(\theta_w D\cdot\nabla C)\ \lambda(\theta_w C\ \rho_b S)$$
$$QC_{\text{in}}\ [\frac{\rho}{\rho}Q\ \frac{\rho_0}{\rho}V\cdot\nabla(\frac{\rho}{\rho_0})]C \tag{4}$$

$$S = K_d C \quad \text{Linear isotherm}$$

$$S = \frac{S_{max} K_L C}{1 K_L C} \quad \text{Langmuir isotherm} \qquad (5)$$

$$S = K_F C^{n} \quad \text{Freundlich isotherm}$$

where

θ_w = water (or moisture) content (dimensionless)

C = aqueous phase concentration (M/L^3)

t = time (T)

ρ_b = bulk density of the medium (M/L^3)

S = solid (or adsorbed) phase concentration (M/M)

V = flow velocity (L/T)

Δ = del operator

D = dispersion coefficient tensor (L^2/T)

κ = decay rate (1/T)

Q = volume flow rate per unit volume of the source or sink (1/T)

$C_{in.}$ = source or sink concentration (M/L^3)

ρ^* = density of injected fluid (M/L^3)

ρ_0 = reference water density (M/L^3)

K_d = distribution coefficient (L^3/M)

s_{max} and K_L (dimensionless) = maximum concentration allowed in the medium and the constant coefficient in the Langmuir nonlinear isotherm, respectively

K_F and n (dimensionless) = coefficient and power constants for Freundlich nonlinear isotherm

The dispersion coefficient tensor D ($L^2 T^{-1}$) in Equation 4 is given as:

$$\theta D = \alpha_T |V| \delta \quad (\alpha_L \quad \alpha_T) \frac{VV}{|V|} \quad \alpha_m \quad \theta \tau \delta \qquad (6)$$

where

$|V|$ = magnitude of V ($L\ T^{-1}$)

δ = Kronecker delta tensor

α_T = lateral dispersivity (L)

α_L = longitudinal dispersivity (L)

α_m = molecular diffusion coefficient ($L^2\ T^{-1}$)

τ = tortuosity (dimensionless)

Model Construction

FEMWATER requires basic hydrogeologic and chemical data for simulations. These basic data include hydraulic conductivity, porosity, hydraulic gradient, initial and boundary conditions, distribution (partition) coefficients, and decay rates. The distribution coefficient, K_d, relates the sorbate and solute for linear isotherms. Distribution coefficients for explosives have been determined (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report").

The modeling domain is defined in three dimensions (Figure 21). In plane view, the domain is bounded by Road 1 North, Chicago Road, and part of Prairie Creek (Figure 17). In the vertical direction, the modeling domain includes the shallow deposit of clay and silt and the weathered bedrock (Figure 21).

The required parameters in FEMWATER include convergence criteria and coefficients of numerical solution techniques. One parameter that controls the amount of leachate entering the unsaturated zone is the infiltration rate. The infiltration rate is usually calculated from precipitation data and soil characteristics. Average annual precipitation at the area near the site is 32-35 in. About 10-12 percent of the annual precipitation is estimated to reach the groundwater reservoir in Illinois (Suter et al. 1959). Another parameter, hydrodynamic dispersion (i.e., the spreading and mixing caused by mechanical dispersion), was introduced into FEMWATER in terms of dispersivity (α). The field values for dispersivity normally are unknown and difficult to obtain. Reported values for dispersivities include 21.3 m longitudinally and 4.27 m transversely for a glacial outwash aquifer in Long Island, NY, which consisted of beds of fine and coarse sand, gravel, and silt (Pinder 1973), and 0.6 m longitudinally for the Bunter Sandstone aquifer near Mansfield, England (Oakes and Edworthy1976). The values for these parameters are strongly scale dependent (Electric Power Research Institute 1985). The dispersivity is a function of site dimensions.

In this application, the following values for dispersivity were used because measured values were unavailable.

$$\alpha_L = 21.3\,m$$
$$\alpha_T = 4.27\,m \qquad (7)$$

In mathematical modeling, adsorption is based on the concept of the retardation factor, R, as:

$$R = \frac{u}{u_s} \qquad (8)$$

where

u = mean water velocity

u_s = mean chemical (solute) velocity ($L\ T^{-1}$)

Hartley and Graham-Bryce (1980) have shown that R (dimensionless) is equivalent to the ratio of total (C_t,M L^{-3}) to dissolved concentration (C_w, M L^{-3}).

$$C_t = \text{Dissolved} \quad \text{Adsorbed}$$
$$C_t = C_w \cdot \phi \cdot S_w \quad C_s \cdot \rho_b \qquad (9)$$

where

C_w = concentration of chemical in the liquid phase

ϕS_w = water (moisture) content (volume of water/bulk volume)

ϕ = porosity (dimensionless)

S_w = water saturation (volume of water/volume of voids)

C_s = concentration of chemical adsorbed to the solid particles (M/M)

ρ_b = bulk density (M L^{-3})

If linear equilibrium adsorption is assumed as described earlier, then the retardation factor, R, due to adsorption is given as:

$$R = \frac{C_w \phi S_w \quad C_s \rho_b}{C_w \phi S_w} = 1 \qquad (10)$$

Hence, the retardation factor is a function of both contaminant property (K_d) and soil (ρ_B,ϕ,S_w) properties. The retardation factor provides a general indication of mobility of the contaminant in the soil. Tables 20 and 21 provide information on

TNT and RDX adsorption coefficients and TNT, TNB, and RDX first-order decay rates, respectively (Pennington et al., "Natural Attenuation of Explosives in Soil and Water Systems at Department of Defense Sites: Interim Report"). The decay rates given in Table 21 were determined from the laboratory batch studies on the LAAP soils. The decay rate used in the model were 10^{-5} 1/day for TNT and TNB and 8.13×10^{-6} 1/day for RDX, which were considerably lower than the batch rates. These decay rates were used based on the model calibration and the fact that the field decay rates are normally lower than the batch rates.

Table 20
Explosives Adsorption Coefficients (K_d, L/kg) for LAAP Aquifer Soils and Regression Coefficient (r^2)

	ML Soil		SP-SM Soil		CL Soil		SM Soil	
Contaminant	K_d	r^2	K_d	r^2	K_d	r^2	K_d	r^2
TNT	0.086	0.73	0.20	0.81	0.37	0.94	0.20	0.77
RDX	0.21	0.95	0.33	0.97	0.33	0.83	0.33	0.95

Table 21
Explosives First Order Decay Coefficient (K^{-1}, hr^{-1}) on LAAP Aquifer Soils and Regression Coefficient (r^2)

	ML (Sandy Silt)		SP-SM (Sandy Silt)		CL (Lean Clay)		SM (Silty Sand)	
Contaminant	K^{-1}	r^2	K^{-1}	r^2	K^{-1}	r^2	K^{-1}	r^2
TNT	0.0006	0.70	0.0006	0.83	0.0014	0.72	0.0007	0.78
RDX	NS	0.06	NS	0.0001	0.0003	0.39	0.00009	0.27
TNB	0.0006	0.83	0.0006	0.63	0.0027	0.74	0.0005	0.38

Note: NS = Not significant.

Model Limitations

Major assumptions and limitations of FEMWATER include the following: (a) single constituent transport, thus intersolute reactions cannot be simulated, (b) abiotic and microbial degradation is treated with a first-order decay model, (c) adsorption coefficient and decay rates can be assigned for different subsurface materials; however, rate constants do not change during simulation time, and (d) contaminant sorption is instantaneous and reversible, and the adsorbed phase is in local equilibrium.

Some of the above assumptions may not be applicable to certain field problems. For this application, the above assumptions were applicable by simplifying some site characteristics required for the modeling without deviating much from actual site conditions. For more details, the reader is referred to FEMWATER model theory documentation (Lin et al. 1997).

Contaminants and Initial Distributions

The modeling domain included the ridge and furrow system area. The modeling focused on the major contaminants, TNT, TNB, and RDX.

Initial conditions of flow and chemical concentration play a major role in the model outcomes. Different numerical techniques available in GMS were compared to establish a realistic initial flow and mass concentration distributions at the site. The initial flow and concentration distribution of TNT, TNB, and RDX were determined using monitoring well data collected in May 1997. The GMS was used to interpolate/extrapolate the data for all points of the numerical mesh system.

Calibration

As described earlier, application of FEMWATER requires knowledge of the spatial distribution of hydraulic conductivity, porosity, boundary conditions, recharge rates, and contaminant concentration. The measurements of hydraulic conductivity are usually too few to fully characterize the heterogeneity of the aquifer and often involve errors and uncertainties. In addition, definitive information about boundary conditions and recharge rates rarely exists because of the complexity of the geology of the aquifer and lack of a reliable means to measure or estimate fluxes at boundaries or recharge rates and their distribution. As a result, numerical flow models are often calibrated by adjusting values of hydraulic conductivity, boundary conditions, and recharge rates and their distribution so that a reasonable match between the simulated and measured hydraulic head is achieved in spite of possible measurement errors. The transport model is also calibrated by adjusting adsorption rates, decay rates, and dispersion parameters to obtain reasonable match between the observed and simulated concentration distribution.

The calibration process is often carried out by manual trial and error, which was the approach employed here. GMS version 2.0 used in this application has an option called Gages, which was used to compare simulated and measured results. This option has been replaced in GMS version 2.1 by a new option called Map Module. Figure 22 illustrates locations of gages (monitoring wells) used in the model calibration. Recently, automatic calibration (inverse) process has been investigated.

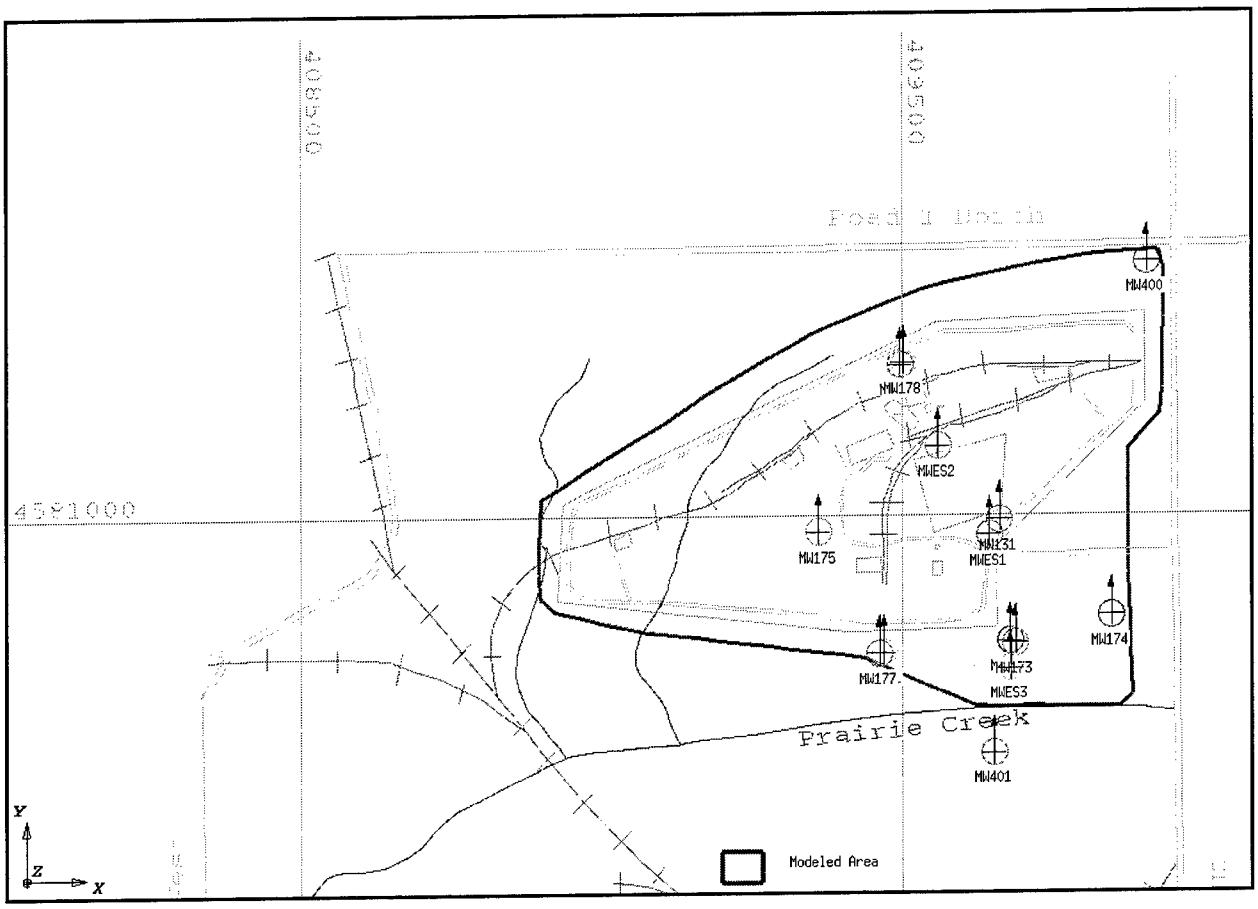


Figure 22. Location of monitoring wells (gages in GMS) tapped in different aquifer layers

Figures 23 through 25 show a comparison between the measured and simulated total head at the selected gages. The difference between the measured and simulated heads at these wells range from zero to about 0.5 m, which is reasonable in view of site heterogeneity. However, at a few locations, the difference between measured and simulated are a few meters. The geologic deposits at the site vary from clays and silt deposits to gravelly sands in the outwash plain, which indicates a very heterogeneous system. The accuracy of the modeling results depends upon availability of detailed hydrogeologic data, particularly sufficient data of the hydraulic conductivity of discrete locations in the subsurface. In this application, only limited data were available, which made the calibration of head and concentration difficult. The results presented here, although with limited calibrations, reproduced the general trends and are acceptable within the model assumptions. The general trend of flow head (m) and velocity (m/day) distribution (Figure 26) shows that the horizontal groundwater flow is towards the Prairie Creek. With more data and calibration, the differences between the observed and simulated results could be further reduced.

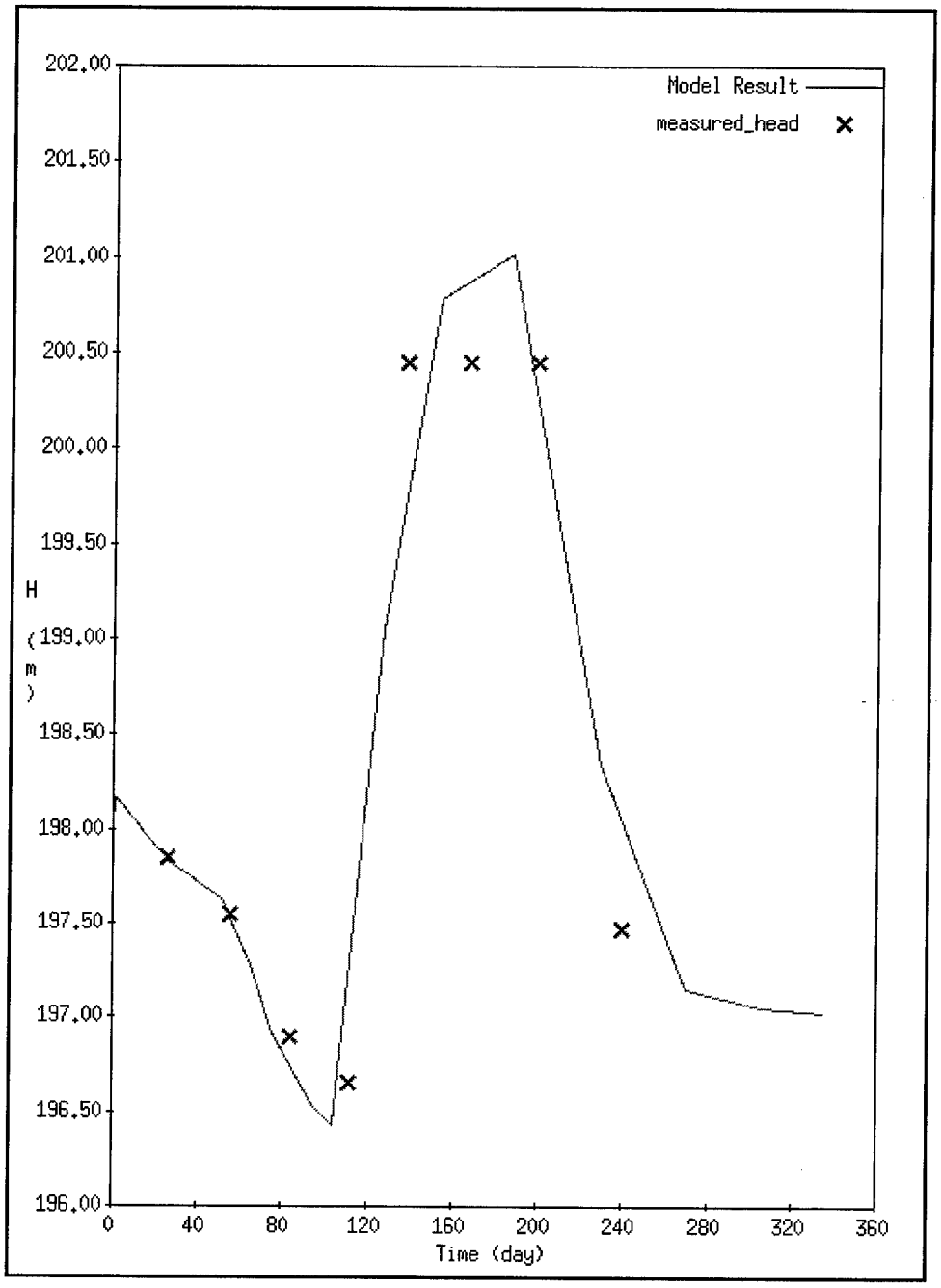


Figure 23. Comparison between measured, x, and simulated head, --- (m, above MS), in MW400 tapped in the overburden aquifer

Predictive Simulations

Prediction requires calculating future flow and transport conditioned on available historical data. The future boundary and other required model conditions are a mathematical statement of certain hypotheses, based on past experiences. The results presented here are based on the following assumptions: (a) no

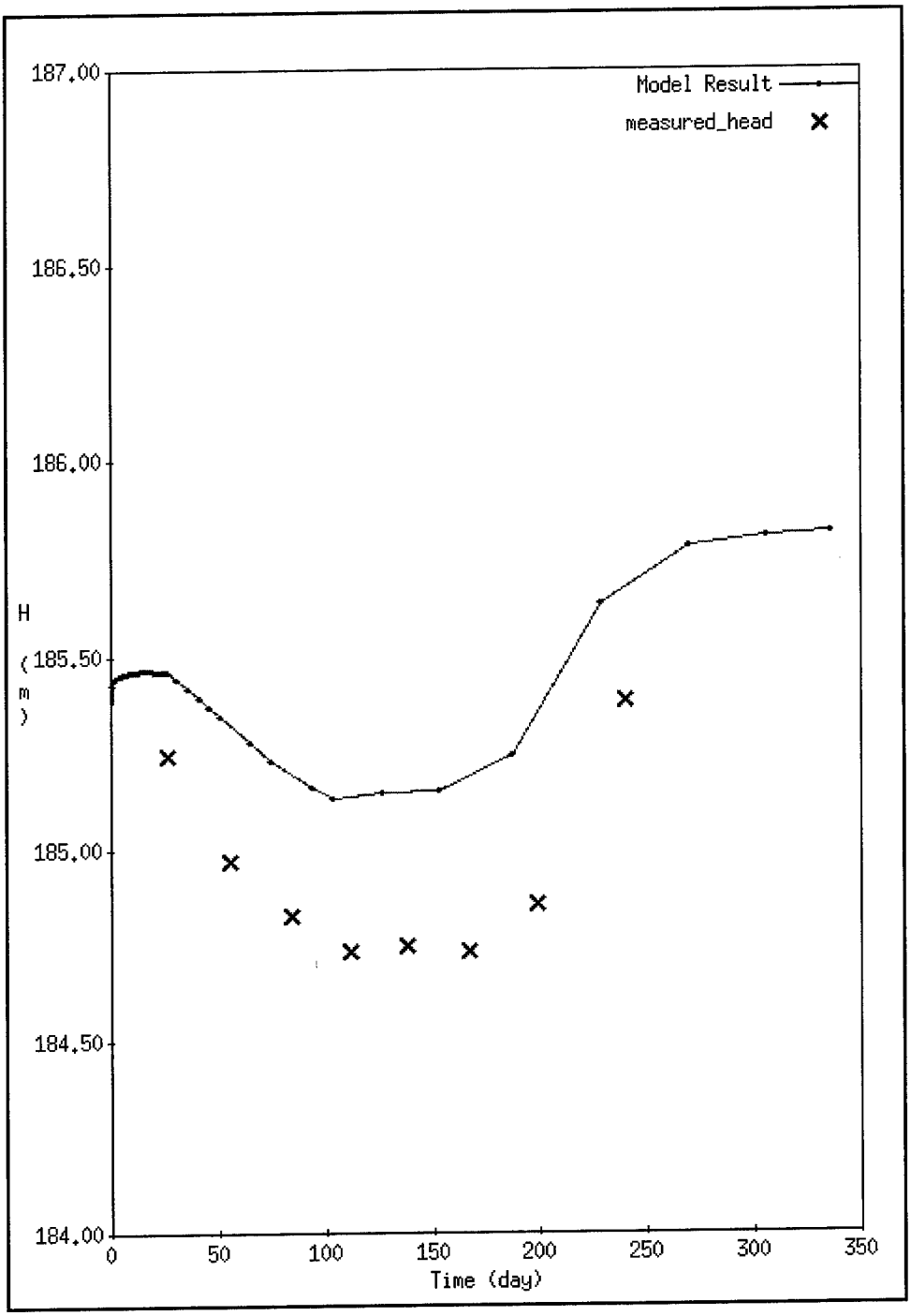


Figure 24. Comparison between measured, x, and simulated head, --- (m, above MS), in MW174 tapped in the overburden aquifer

additional source of contamination is added into the site, (b) infiltration rate stays constant throughout the simulations, (c) flow boundary conditions recur every year, and (d) no recharge or discharge through pumping occurs during the simulations. The predicated results should be updated and adjusted as new data become available. Jorgensen (1981) illustrates an iterative way in which a model prediction may be improved as new information is obtained.

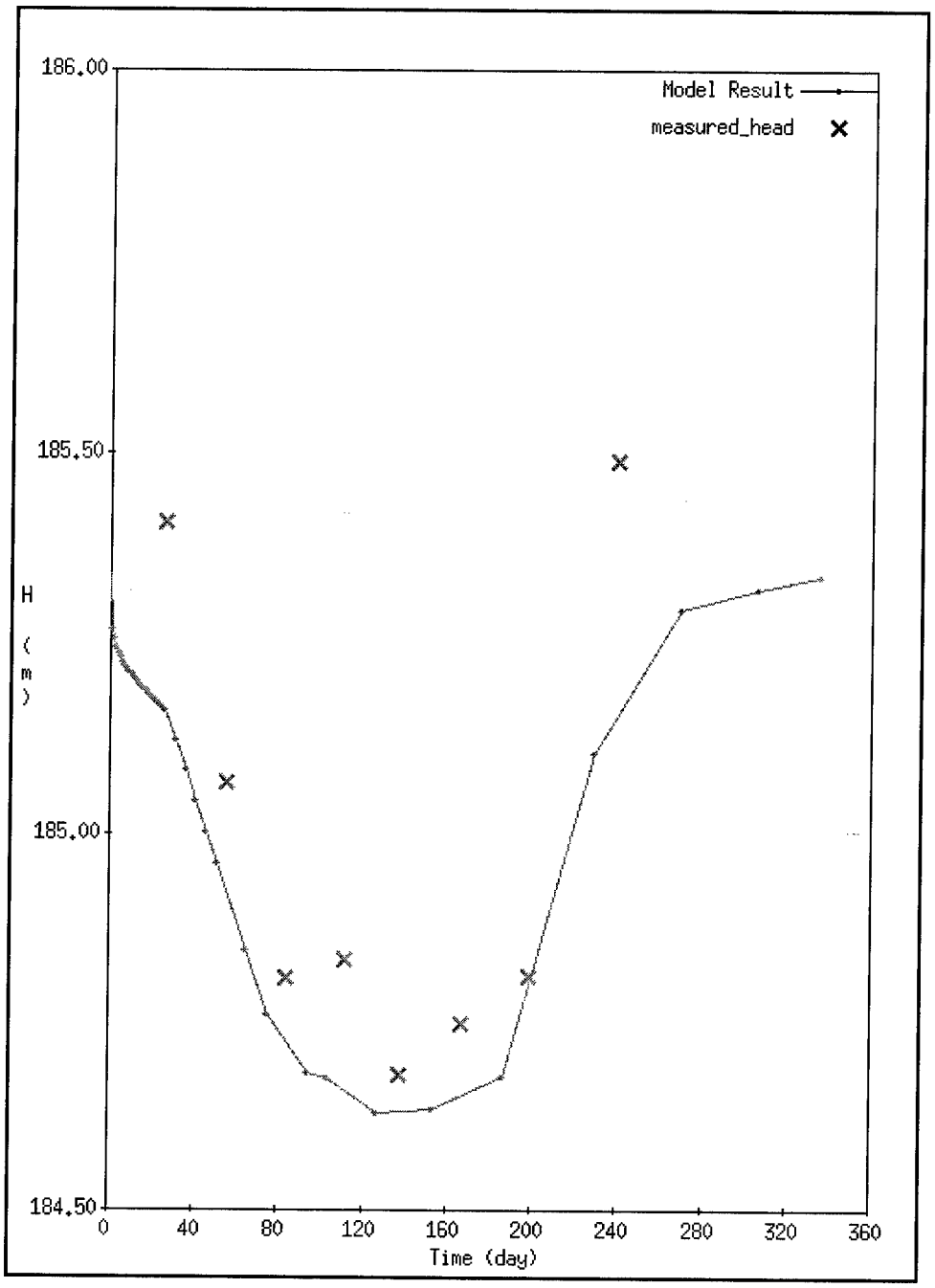


Figure 25. Comparison between measured, x, and simulated head, --- (m, above MS), in MW177 tapped in the bedrock aquifer

When comparing the simulation for 20 years to the initial conditions (May 1997), the TNT, TNB, and RDX plumes are virtually static to diminishing (Figures 27 through 32). The reduction of TNT and TNB plumes' concentration is slightly higher than the RDX.

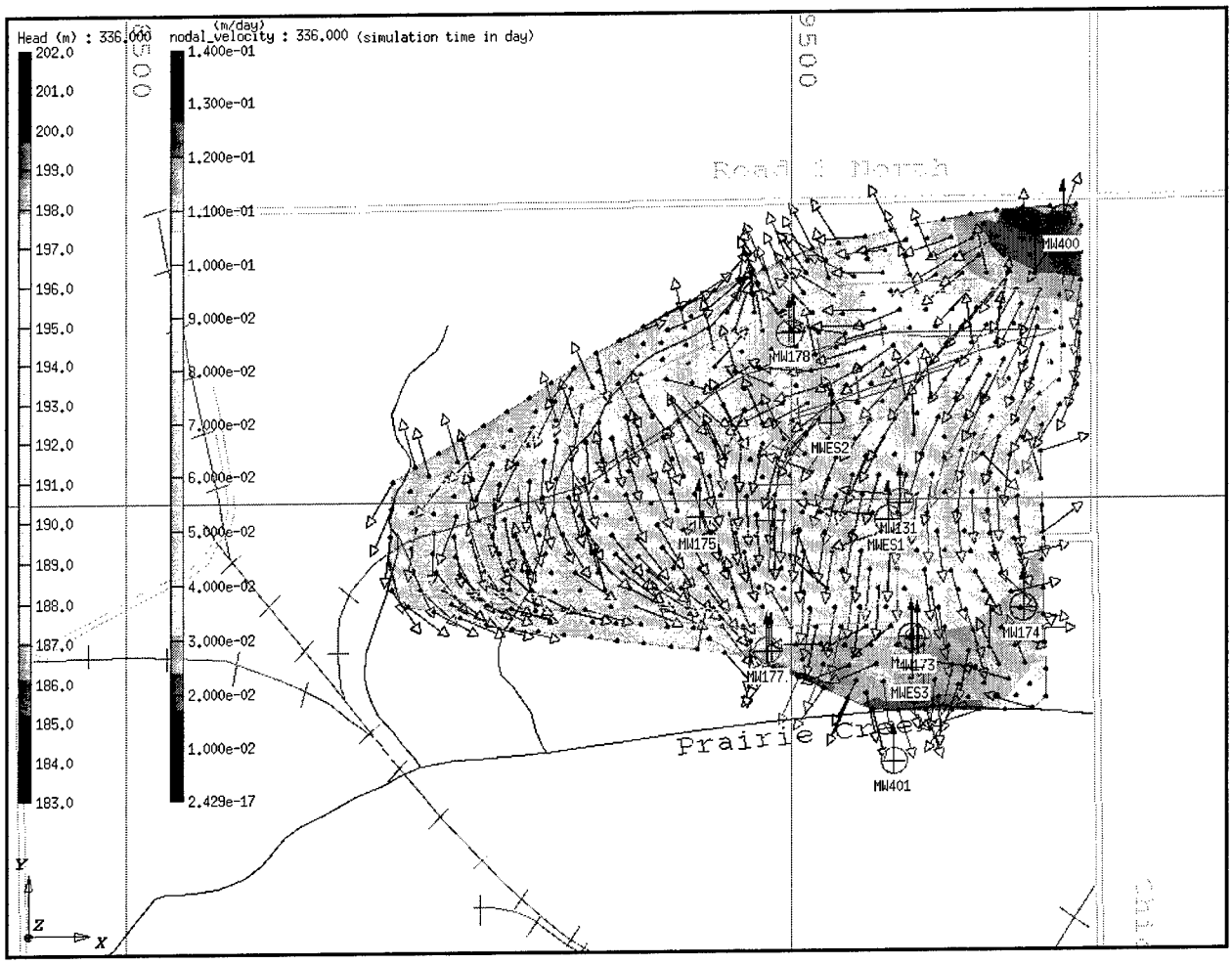


Figure 26. Simulated distribution of total head (m) and velocity at time = 336 days

Summary and Conclusion

The subsurface at Site L1 consists of two aquifer systems: the shallow overburden aquifer and the deep dolomite bedrock aquifer. The bedrock aquifer has fractures and solution cavities (Dames and Moore, Inc. 1993). Flow through conduits does not obey Darcy's Law, upon which the model was based. Groundwater flow through fractured media can be much faster and follows preferential pathways compared with flow in porous media. The calculations presented here are based on the assumption that the bedrock behaves as a porous medium.

The hydraulic conductivity of overburden and bedrock aquifers at the JAAP ranged from 1.5×10^{-6} cm sec^{-1} to 1.8×10^{-2} (Dames and Moore, Inc. 1993).

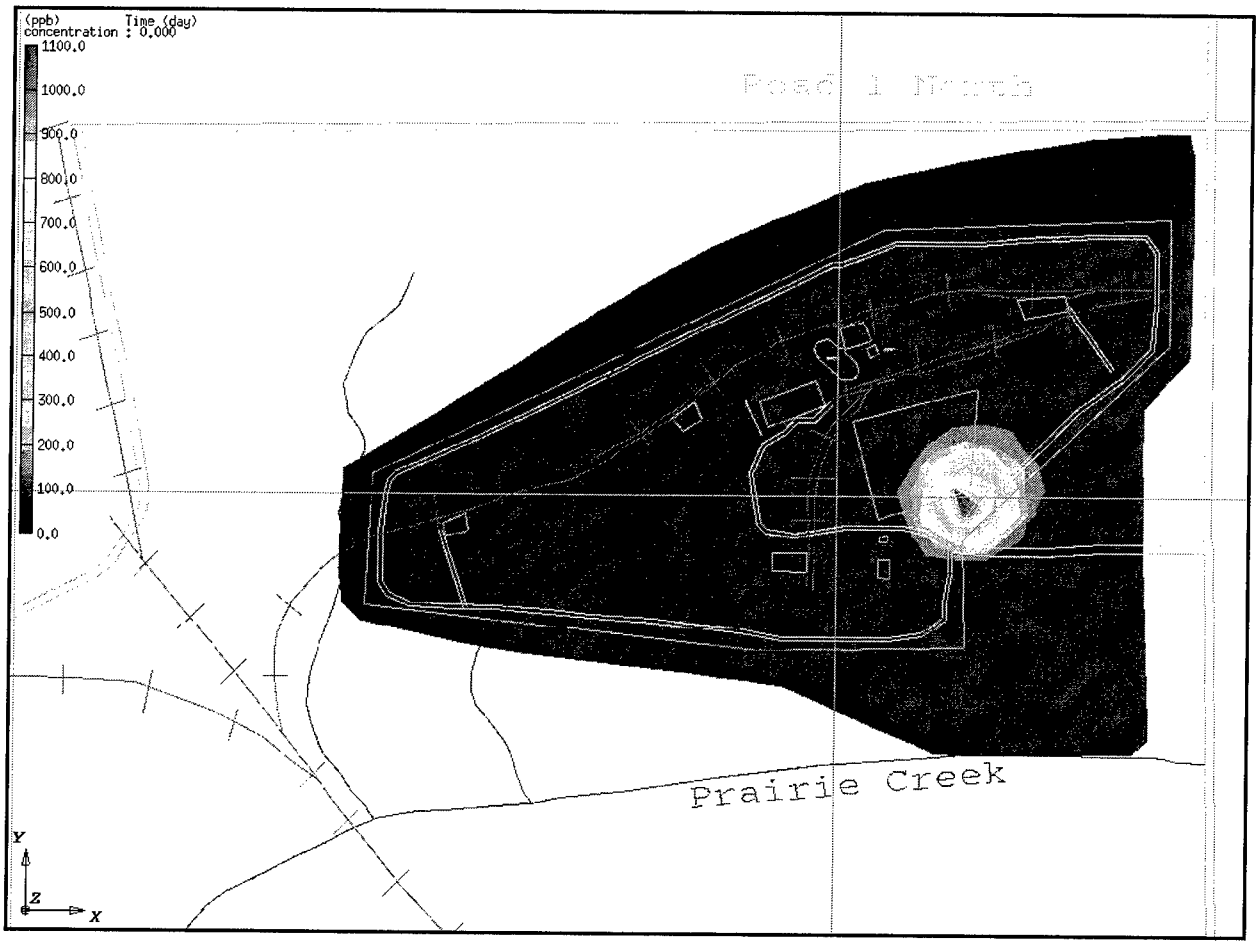


Figure 27. Initial (May 1997) distribution of TNT concentration

The geologic deposits at the site vary from clays and silt deposits to gravelly sands in the outwash plain, which indicates a very heterogeneous system. The accuracy of the modeling results depends upon availability of detailed hydrogeologic data, particularly sufficient data of the hydraulic conductivity of discrete locations in the subsurface. In this application, only limited data were available, which made the calibration of head and concentration difficult. The modeling results, however, are acceptable since the general trends of flow and plumes were reproduced.

The measured and simulated flow data indicate slow subsurface flow at Site L1 due to the low permeability media and hydraulic gradients. The groundwater flows toward Prairie Creek. The shallow groundwater discharges into Prairie Creek.

The simulated concentrations of TNT, TNB, and RDX indicate static and diminishing plumes (Figures 27 through 32). The reduction rate of RDX plume is lower than the rates for TNT and TNB plumes.

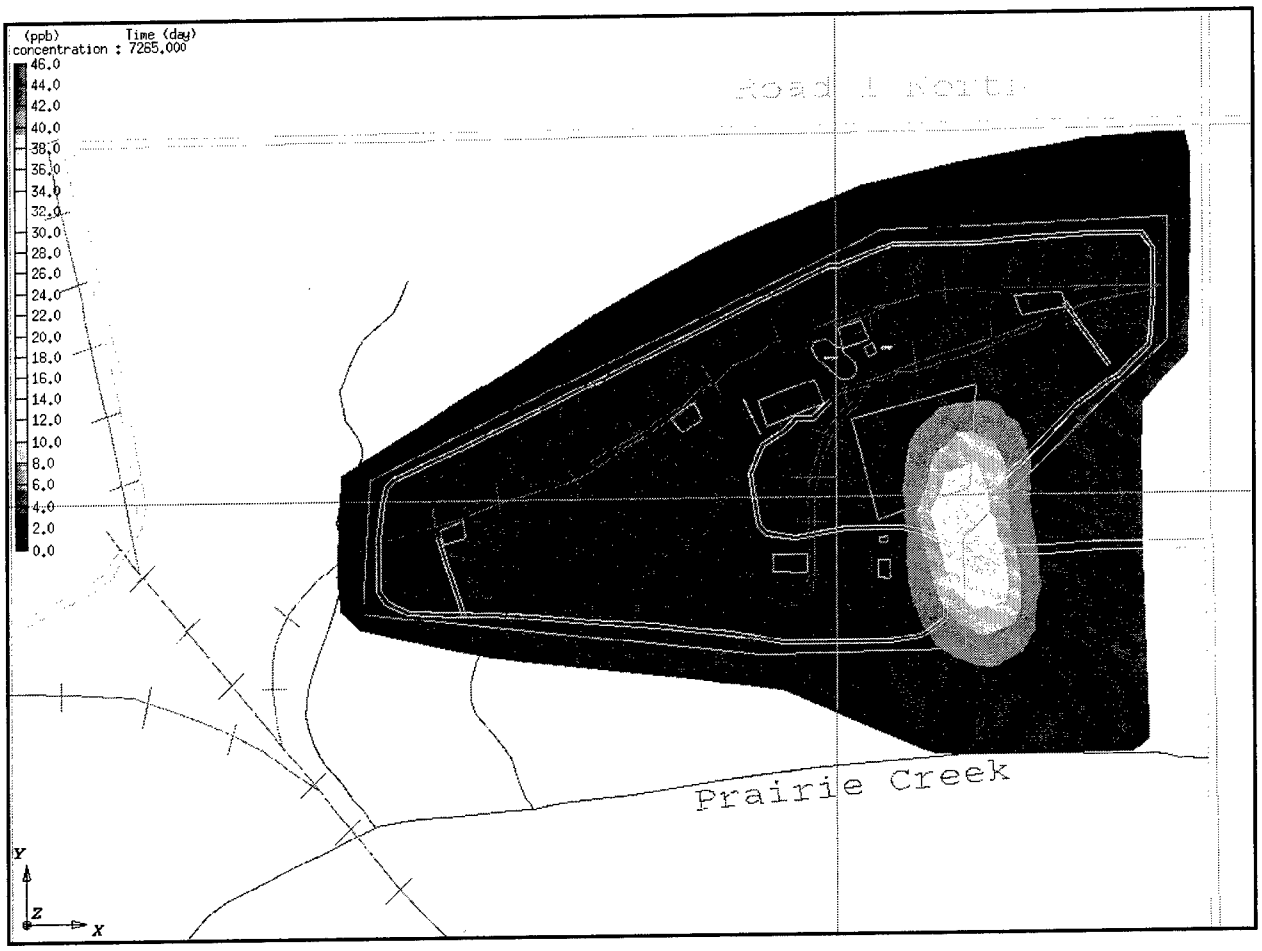


Figure 28. Predicted distribution of TNT plume after 20 years

The results presented here are bounded within the assumptions and limitations of the selected model. The model approximately simulated the general behavior of flow and the plume at the site. The predicted results should be adjusted, and the calibration processes should be repeated as new data become available.

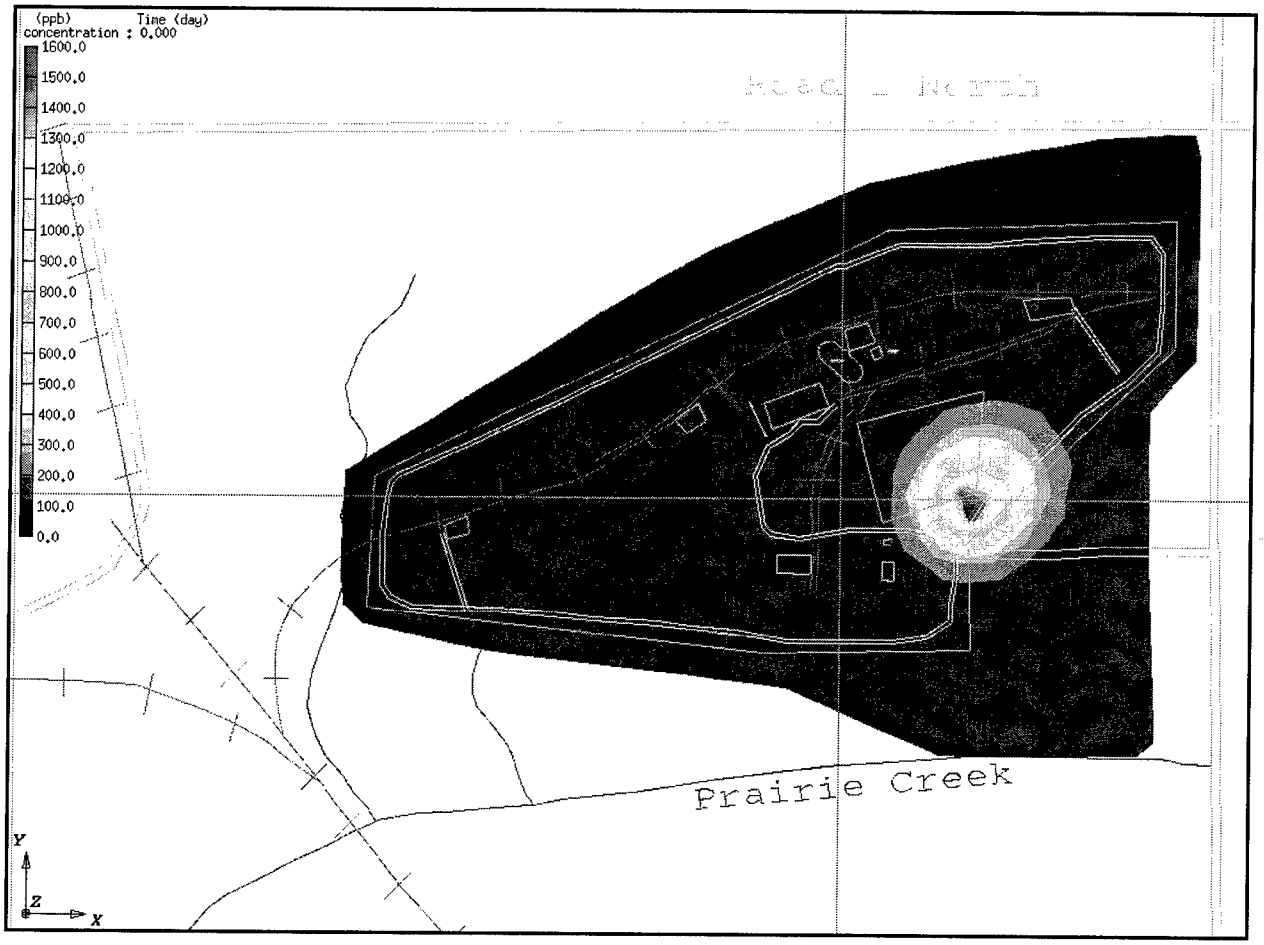


Figure 29. Initial distribution of TNB concentration (May 1997)

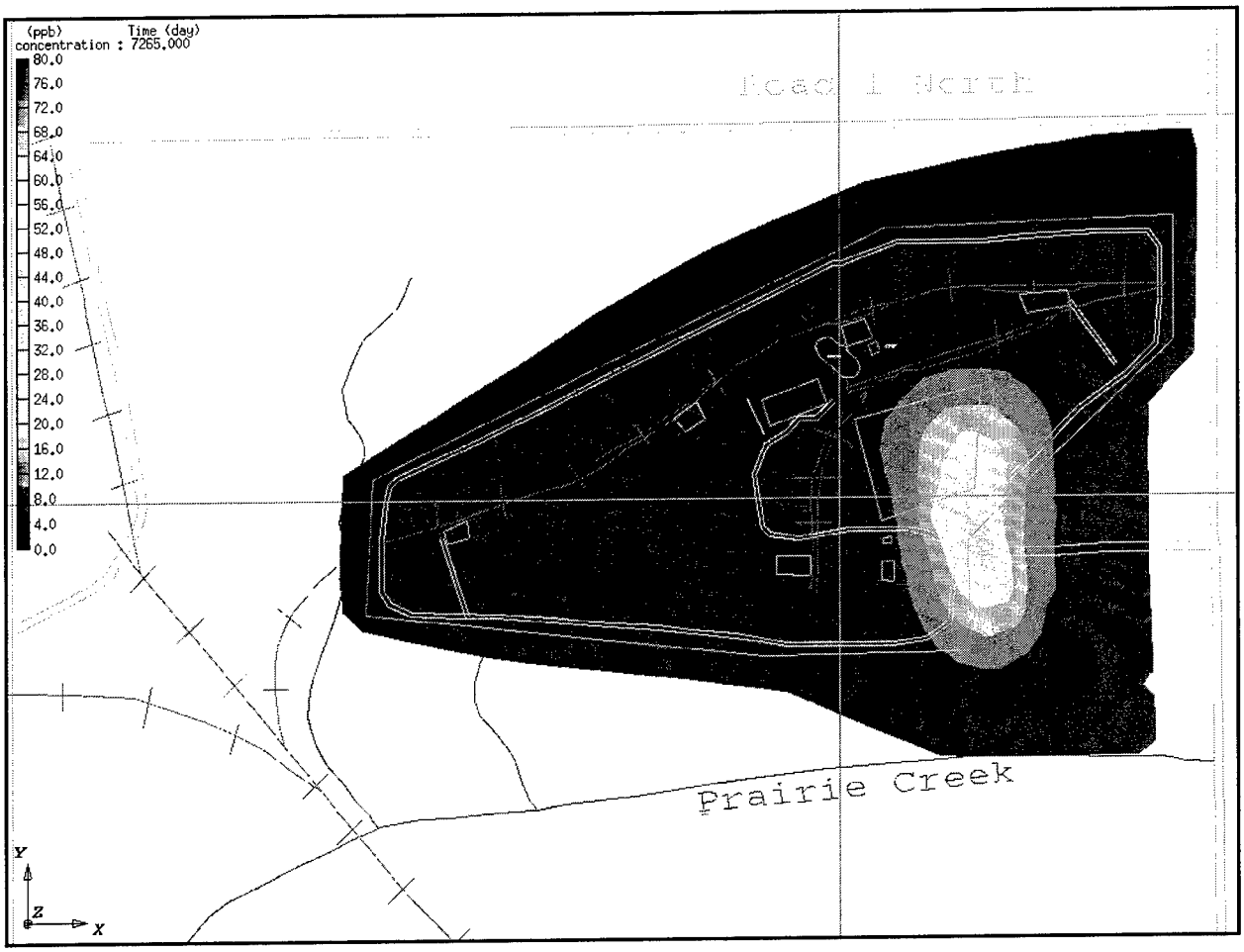


Figure 30. Predicted distribution of TNB plume after 20 years

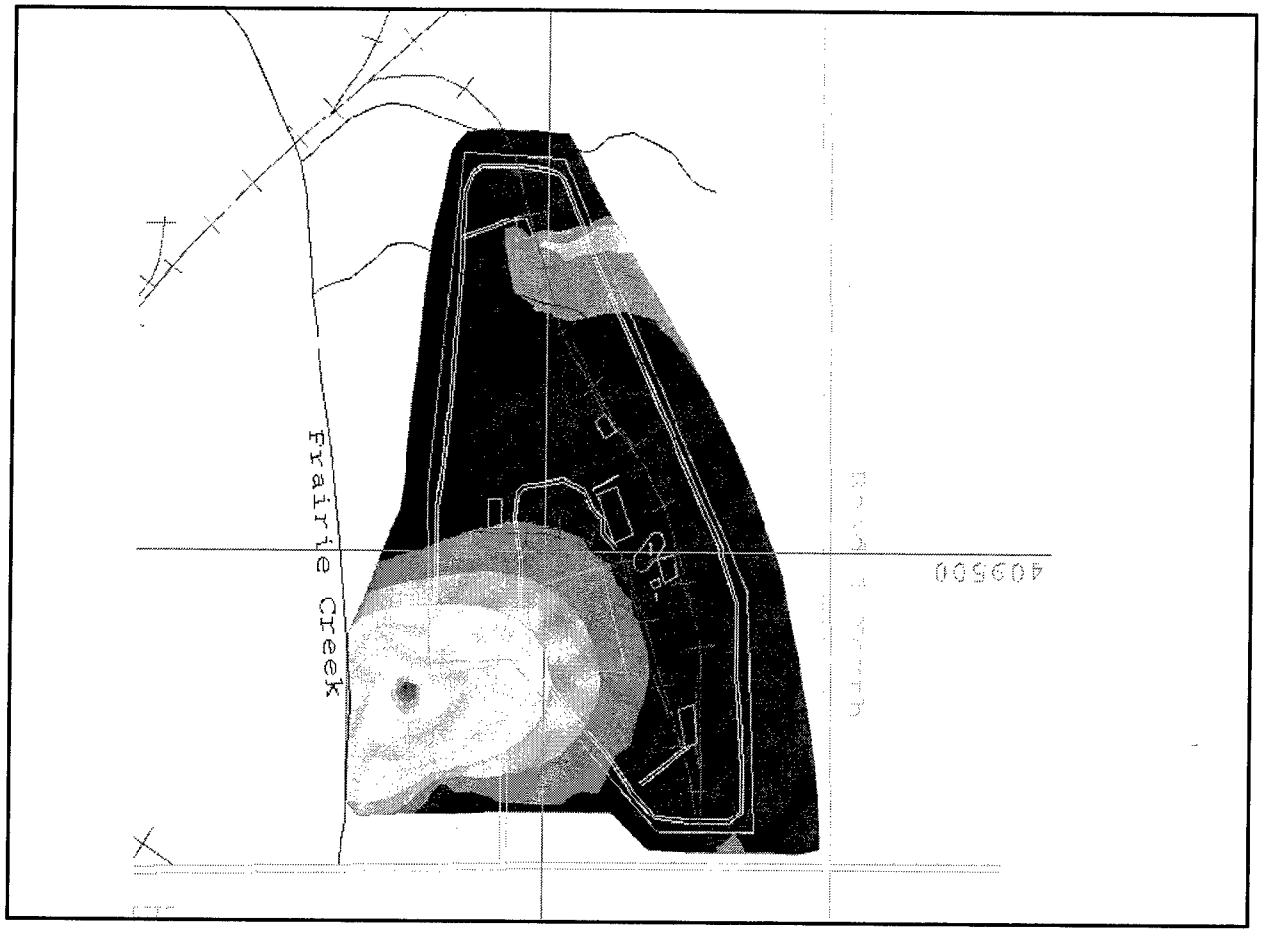


Figure 31. Initial distribution of RDX concentrations (May 1997)

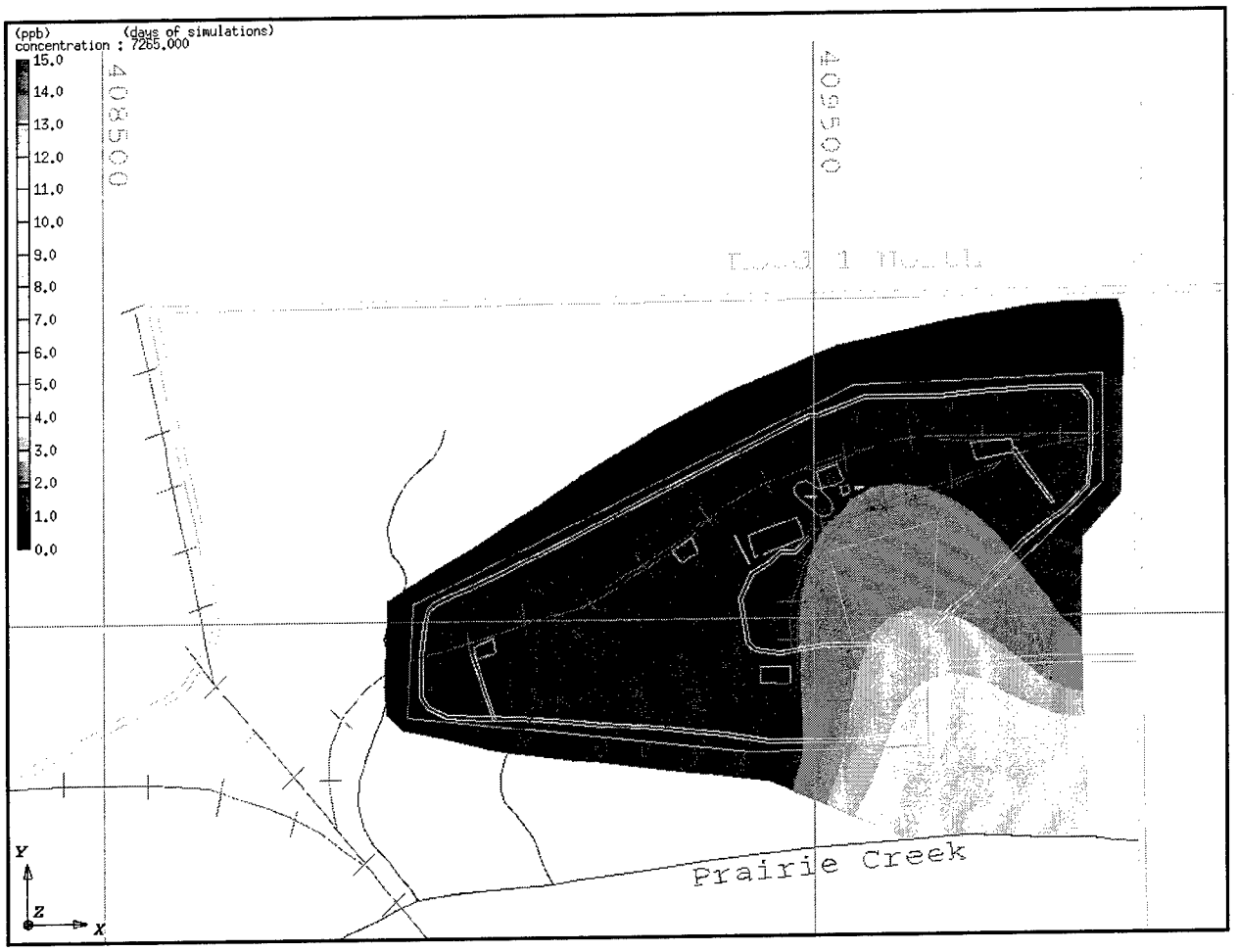


Figure 32. Predicted distribution of RDX concentration after 20 years

6 Conclusions

Analyses of historical plus current data resulted in few statistically significant trends. In the first nine sampling rounds, only five wells exhibited significant explosives concentrations. Four of these showed significant trends for some analytes. TNT and TNB were decreasing in two wells; TNB was increasing in one well; RDX was decreasing in one well. In the few instances where trends were significant, the most prominent contaminants (TNT, RDX, and TNB) were generally decreasing. Trends for two-thirds of the significant trends for explosives-related degradation products (4ADNT, 2ADNT, 2,6DNT, and DNA) were increasing. In the other one-third, these analytes were decreasing.

Monitoring Well MW131 exhibited significant increases in TNT, 3,5DNA, TNB, 4ADNT, 2ADNT, and DNB in sampling Round 9. The concentration of TNT increased from a mean of $1{,}505 \pm 67\ \mu g\ L^{-1}$ in Rounds 1 through 8 to $6{,}830\ \mu g\ L^{-1}$ in Round 9. These unexpected increases prompted an additional limited sampling round in March 1998. Results showed a further elevation in TNT and other analytes in MW131. The TNT concentration increased to $12{,}130\ \mu g\ L^{-1}$. These data suggest that short-term monitoring is insufficient to define trends in contaminant concentration at the site.

A cone penetrometer sampling event was conducted to refine the definition of site lithology and to secure samples for a biomarker project funded by the Strategic Environmental Research and Development Program. Explosives were detected in only 7 of the 56 samples collected from various depths across the site. At three locations, samples were collected at several depths for the biomarker research. Results indicated that the site possesses the potential for slow mineralization of TNT and RDX. Requisite genes were detected; site conditions were appropriate for supporting microflora; and the existing microbial community structure exhibited a healthy diversity.

A conceptual model for the site showed very slow-moving flow. Predictions for TNT and RDX show a static to gradually diminishing plume. The locations of the plume centers for TNT and RDX coupled with the generally higher concentrations of TNT relative to RDX suggest that RDX has migrated further and that only limited residuals remain on the site. The TNT plume has not migrated very far from the original source and seems virtually static. These observations may be evidence of a "climax" environment that has little potential

for future change, barring future releases of explosives such as those observed in January and March 1998 in MW131.

The principal objective of this study was to demonstrate whether or not natural attenuation is occurring at Site L1. Results of trend analyses of historical data plus groundwater monitoring data and the model prediction of a static to slowly diminishing plume for TNT, RDX, and TNB satisfy the first line of evidence set forth in the EPA policy statement on natural attenuation; contaminant concentration is slowly declining over time. Results of biomarker studies both in microcosms and in situ support the second and third lines of evidence set forth in the EPA policy statement. The potential for a slow microbial mineralization mechanism for TNT and RDX degradation was demonstrated. Estimated degradation rates were 0.127 ± 0.030 and 0.194 ± 0.020 percent per day for TNT and RDX, respectively. All of these results indicate that natural attenuation is occurring and is causing declining concentrations in explosives over time. However, data generated for MW131 in sampling Rounds 9 and 10 suggest that the subsurface hydrogeology and contaminant distribution is not sufficiently defined to anticipate long-term release of contamination. Therefore, natural attenuation cannot be confirmed as a remedial alternative until the elevated explosives concentrations at MW131 are explained and taken into account. A possible cause of the elevated concentrations is atypically high precipitation that mobilized a previously stable source of explosives. If this source is in the ridge and furrow system, which is slated for active removal, future such elevated concentrations are unlikely. Intervention of contaminant migration by the cottonwood trees may also reduce the potential for future environmental hazard. If the Rounds 9 and 10 data for MW131 can be explained and the explanation reveals that source removal, phytoremediation, and/or other factors will ensure future protection of environmental receptors, natural attenuation will be a viable long-term option for Site L1.

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Appendix A
List of Symbols

θ = moisture content, dimensionless

θ_r = residual moisture content, dimensionless

ϕ = porosity, dimensionless

h = pressure head, L

h_b = bubbling or air-entry pressure, L

δ = Kronecker delta tensor

κ = decay rate constant (1/T)

λ = pore size distribution, dimensionless

Kr = relative hydraulic conductivity, dimensionless

$C_m(h)$ = water content, dimensionless

θ_w = moisture content, dimensionless

C = aqueous phase concentration, M/L^3

t = time, T

ρ_b = bulk density of the medium, M/L^3

S = solid, or adsorbed phase concentration, M/M

V = flow velocity, L/T

∇ = del operator

D = dispersion coefficient tensor, L^2/T

Q = volume flow rate per unit volume of source or sink, 1/T

C_{in} = source or sink concentration, M/L^3

ρ^* = density of injected fluid, M/L^3

ρ = fluid density, M/L^3

ρ_0 = reference water density, M/L^3

K_d = distribution coefficient, L^3/M

S_{ma} = maximum concentration allowed in the medium isotherm, M/M

K_L, K_F, n = constant coefficients and power for Langumir and Freundlich isotherm, dimensionless

α_L, α_T = longitudinal and lateral dispersivity coefficients, L

α_m = molecular diffusion coefficient, L^2/T

$|V|$ = magnitude of velocity, V, L/T

δ = Kronecker delta tensor, dimensionless

τ = tortuosity, dimensionless

R = retardation coefficient, dimensionless

u = mean water velocity, L/T

u_S = mean chemical (solute) velocity, L/T

C_{total} = total concentration, M/L^3

C_w = concentration of chemical in liquid phase, M/L^3

C_S = concentration of chemical adsorbed to solid particles, M/L^3

Sw = moisture content, volume of water/bulk volume